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THE LIGHT AGEING OF POLYMETHYLMETHACRYLATE—I. THE KINETICS OF GAS EVOLUTION AS AFFECTED BY LIGHT OF VARYING WAVELENGTH. THE QUANTUM YIELD OF PHOTODEGRADATION*

M. I. FROLOVA and A. V. RIABOV

(*Received* 15 *April* 1958)

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LIGHT ageing appears to be one of the chief causes of the degradation under working conditions of articles made of polymeric materials.

The extensive use of plastic materials in various branches of the national economy as coatings and substitutes for metals, glass components and other products leads to the necessity for a detailed study of the physicochemical processes which cause ageing and the development of means for preventing it.

The important divisions in the study of the general question of the light ageing of polymers appear to be:

(1) determination of the wavelength of light which has an effect on polymeric materials and

(2) an estimate of the quantum yield of photodegradation.

The fundamental condition of photochemistry asserts that radiation can affect a substance only in that case where it is capable of absorbing the incident energy. Depending on their composition and structure polymeric materials absorb energy in different spectral ranges in which, consequently, they also undergo ageing [1–9]. Light ageing of rubber, a survey of which is in the book by Kuz'minskii *et al.* [10], has been extensively studied.

The size of the quantum yield of the light reaction can give an immediate indication of the nature of the processes taking place. The presence of oxygen plays a substantial role in this [7,11,12].

From data in the literature [13,14] it is known that polymethylmethacrylate absorbs ultra-violet light up to 3300Å; therefore it was to be expected that ultra-violet light on the polymer in question promotes photochemical reactions.

We investigated the kinetics of gas evolution during the irradiation of polymethylmethacrylate by light of varying wavelength and the quantum yield of photodegradation. All the experiments were carried out in the absence of oxygen.

* Vysokomol. soedin. **1**: No. 10, 1453–1456, 1959.

EXPERIMENTAL

The experiments for studying the kinetics of gas evolution from polymethylmethacrylate on irradiation with light of varying wavelength were carried out on polymethylmethacrylate powder obtained from an industrial sheet of the organic glass. A shaving of the sheet of organic glass was dissolved in acetone and the polymer precipitated by water; this operation was carried out 3 times. The dried polymer was ground in a porcelain mortar and sieved through a screen. We used for the experiments polymethylmethacrylate powder of diameter 0·5 to 1 mm.

The irradiation of the polymer was carried out in a quartz test-tube 25 mm in diameter and 25 cm in length, which was connected by means of a ground glass joint to an all glass high-vacuum system provided with a McLeod gauge. In each experiment 5 g of polymer were taken for irradiation. The powder was put in the test-tube and distributed in it longitudinally for 20 cm. During the experiments the volume of the system was constant. The temperature of the experiments was $25 \pm 0{\cdot}5°$.

A thermopile calibrated in V/W correct to 10 per cent was used for estimating the intensity of the ultra-violet radiation of varying wavelength, the e.m.f. reading of which was measured by means of a direct current type PP potentiometer. The thermopile was put on the surface of the middle part of the test-tube and its e.m.f. was constant in all the experiments concerned with the study of the effects of ultra-violet light of varying wavelength.

Uniformity of exposure during the irradiation by light of varying wavelength was achieved by movement of the light source—a PRK-2 mercury lamp (emitting in the ultra-violet range from 2483 to 3663 Å). A stabilizing voltage was applied to the PRK-2 lamp (a CN-2 voltage stabilizer).

A silicate glass 5 mm in thickness, which conducts visible light well but stops rays in the region of 3500 Å, and "Pyrex" glass, which is transparent to waves up to about 3000 Å, were used as filters.

Before each experiment the system was tested, after which the polymethylmethacrylate powder was evacuated to a pressure of the order of 10^{-6} mm Hg over the course of 25–30 hr. We considered the degasification sufficient if on disconnecting the system from the pump the pressure did not increase after a 2-hr test. At the end of the evacuation the powdered polymer was exposed to irradiation. In the determination of the quantum yield which was calculated from the amount of gaseous products evolved, a film of the polymer was exposed to radiation, not powder. The film of polymethylmethacrylate was obtained by dissolving the thrice precipitated polymer in benzene, pouring this solution on to a strictly horizontal surface of silicate glass and the slow removal of the solvent by evaporation.

Films 0·08–0·09 mm in thickness were used for an experiment, and as a light filter a 15 mm thickness was used of an aqueous solution of potassium chromate

and *para*-nitrosodimethylaniline [15] poured into a small dish with UFS-2 glasses which virtually allow no passage of infra-red radiation.

The film of polymethylmethacrylate was placed in a quartz test-tube, carefully evacuated to a high vacuum and then subjected to irradiation. The exposure in front of, and behind, the film was determined by means of the thermopile. Correspondingly the gas pressure of the system was also determined by means of the McLeod gauge.

EXPERIMENTAL RESULTS

TABLE 1. CHARACTERISTICS OF THE PHOTOLYSIS OF POLYMETHYL METHACRYLATE BY THE ACTION OF ULTRA-VIOLET RADIATION

Irradiation time (min)	Pressure of evolved gases on irradiation (in mm Hg $\times 10^2$)		
	without filter	with silicate glass	with Pyrex glass
0	0	0	0
10	7·27	0·1	0·6
20	14·3	0·3	1·6
30	19·8	0·3	2·6
40	26·2	0·3	3·1
50	34·6	0·6	4·1
60	37·1	0·6	4·4

Data on gas evolution during the irradiation of polymethylmethacrylate by ultra-violet light of varying wavelength are shown in the Table. These data are also presented in Fig. 1 in the form of a graphic relationship of gas being evolved with time.

From the Table and graph it is seen that an evolution of gaseous products, which indicates the presence of photolytic processes, occurs during the irradiation of polymethylmethacrylate by ultra-violet light of wavelength less than 3500 Å. No marked increase in the gas pressure of the system is observed during the irradiation of polymethylmethacrylate by light of wavelength greater than 3500 Å. It should be noted that the evolution of gaseous products ceases immediately after turning off the light source.

The quantum yield was calculated from the number of moles of gas formed per primary mole of polymer and from the number of quanta absorbed by a mole of polymer. The number of moles of gas evolved per primary mole of polymer is $0{\cdot}9 \times 10^{-5}$. The number of quanta absorbed by one mole of polymer is $0{\cdot}24 \times \times 10^{-23}$. The quantum yield for rays of wavelength 3030–3130 Å is $0{\cdot}23 \times 10^{-3}$.

The results quoted in the present work are the arithmetical mean of 4–5 determinations, the variation of individual determinations from the average value being not greater than 5 per cent.

In conclusion we express our gratitude to Academician V. A. Kargin for valuable advice on the organisation and carrying out of the work presented.

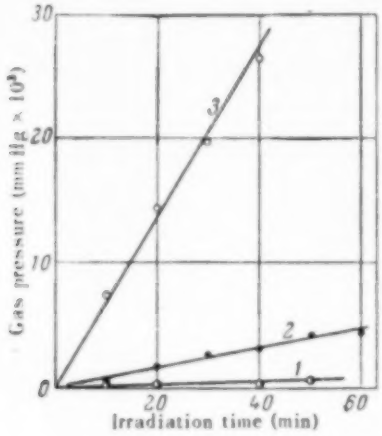

FIG. 1. Kinetics of the evolution of gaseous products during the irradiation of polymethylmethacrylate in vacuum. (1) Silicate glass filter; (2) "Pyrex" glass filter; (3) No filter.

SUMMARY

(1) It is shown that photolysis of polymethylmethacrylate takes place on irradiation with ultraviolet light of wavelength less than 3500 Å.

(2) The quantum yield of the photodegradation process calculated on the basis of the volatile products evolved is $0{\cdot}23 \times 10^{-3}$.

(3) The low quantum yield and the cessation of gas evolution after shutting off the light source leads to the assumption of a non-chain nature for the photolysis of polymethylmethacrylate irradiated in vacuum.

Translated by R. G. P. TOWNDROW

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THE POLYMERIZATION OF DIMETHYLALLYLSILANE AND METHYLPHENYLDIALLYLSILANE ON A ZIEGLER CATALYST*

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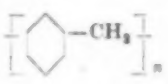
Institute of High Molecular Compounds

(*Received* 17 *May* 1959)

A NUMBER of works have appeared recently [1–6] concerned with the *cyclo*-polymerization of non-conjugated dienes. The following chain structure was suggested for the polymers obtained:



The six-membered ring may consist either of carbon atoms [6] or may also include hetero-atoms [1–5].

Similar polymers were obtained by Butler [1] from diallyl substituted quaternary ammonium bases. Marvel and Vest [2] obtained polymers with rings in the primary chain from α, α' -dimethylenepimelic acid and its derivatives. Jones synthesized analogous polymers from diacrylmethane [3] acrylic anhydride [4] and alloöcimene [5]. The usual initiators were used in all the works listed [1–5]. The possibility of obtaining *cyclo*-polymers by means of complex organometallic catalysts was shown by Marvel and Stille [6] in the cases of 1,6-heptadiene, 1,5-hexadiene and 2,5-dimethyl-1,5-hexadiene. The small amount of unsaturation or its complete absence in the polymers, complete solubility in benzene, carbon tetrachloride, etc., is evidence for the suggested chain structure.

In the present work an investigation was carried out on the polymerization of diallyl substituted silanes. In the polymerization of diallylsilanes using radical initiators [7, 8] either low-molecular oily polymers or three-dimensional polymers were obtained. In the above-mentioned work of Petrov [7] the possibility of polymerizing dimethyldiallylsilane and methylphenyldiallylsilane was established. Solid, three-dimensional polymers of both these monomers were obtained by him at a pressure of 5500 atm and 130° using *tert*-butyl peroxide as initiator. In polymerizing dimethyldiallylsilane on the Ziegler catalyst of Topchiev *et al.* [9] we obtained a mixture of polymers, the bulk of which consisted of liquid products. The structure of the polymers obtained was not established.

* Vysokomol. soedin. 1: No. 10, 1469–1472, 1959.

The polymerization of dimethyldiallylsilane and methylphenylsilane was carried out on a Ziegler catalyst in *n*-heptane at 70–80°, the concentration of monomer in solution being 10 to 50 per cent and the molar ratios of $Al(C_2H_5)_3$: $TiCl_4$ being from 3 : 1 to 1 : 1.

The quantity of titanium tetrachloride we used was 3 per cent by weight of the monomer. The dimethyldiallylsilane polymers (Table 1) were solid, rubbery products 80–100 per cent soluble in benzene at room temperature. In the soluble portion 20–25 per cent was found of units containing double bonds.

TABLE 1. POLYMERIZATION OF DIMETHYLDIALLYLSILANE ON TRIETHYLALUMINIUM TITANIUM TETRACHLORIDE CATALYST

Concentration of monomer in solution (%)	Molar ratio $\frac{Al(C_2H_5)_3}{TiCl_4}$	Temperature °C	Duration of experiment (hr)	Polymer yield (%)	Solubility of polymer in benzene (%)	Amount of units containing double bonds (%)	$[\eta]$ at 20° in benzene
10·8	1:1	80	26	16·8	73·5	21	—
10	1:1	80	24	12·5	90	20	—
10	1:1	80	24	16·7	82	19	—
20	1:1	80	24	16·7	84	21	—
20	1:1	80	24	18	86·6	20	—
44·8	1:1	80	23	73·6	83·6	19	0·051
50	1:1	80	24	41·8	83·6	21	0·055
64·8	1:1	80	21	65	100	26	0·098
10	2:1	80	41	19	81	25	0·094
24·3	2:1	80	23	70·5	100	23	0·076
42·5	2:1	80	23	84	100	25	0·069
22·5	3:1	70	26	5·4	100	23	—
37·6	3:1	70	21	5·8	95	20	—
50	3:1	80	41	45	97·5	23	—

The characteristic viscosity in benzene varied from 0·05 to 0·09. The glass temperature of the soluble portion of the polymer was from −6° to −15°.

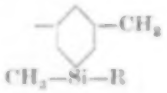
The methylphenyldiallylsilane polymers (Table 2) were white powdery materials. The solubility in benzene at room temperature is 70–100 per cent. The characteristic viscosity of the soluble portion in benzene is 0·04–0·08. Eighteen to 40 per cent of units containing double bonds were found in the polymer, depending on the ratio of the components in the catalyst. The least unsaturation was possessed by polymers obtained with an $Al(C_2H_5)_3 : TiCl_4$ ratio greater than unity.

The dimethyldiallylsilane and methylphenyldiallylsilane polymers have an elementary composition identical to the original monomers.

Table 2. Polymerization of methylphenyldiallylsilane on triethylaluminium titanium tetrachloride catalyst

Concentration of monomer in solution (%)	Molar ratio $Al(C_2H_5)_3$ $TiCl_4$	Temperature (°C)	Duration of experiment (hr)	Polymer yield (%)	Solubility of polymer in benzene (%)	Units containing double bonds (%)	[η] at 20° in benzene
10	1:1	80	89	28	68	25	—
28	1:1	70	30	30	71·6	40	0·042
30	1:1	80	24	60·2	67	36	0·067
50	1:1	80	24	78	100	38	0·085
10	2:1	80	89	20	91·5	21	0·063
26·8	2:1	80	23	46·2	100	24	0·065
50	2:1	80	24	62	100	25	0·064
33·7	3:1	80	24	9	98	18	—

It may be considered that the unit



predominates in the structure of polydimethyldiallylsilane and polymethylphenyldiallylsilane (where R is CH_3 or C_6H_5) analogous to the chain unit of the above-mentioned non-conjugated dienes.

EXPERIMENTAL

Dimethyldiallylsilane was obtained by Iavorski's method from dimethyldichlorosilane and allyl bromide; yield 63 per cent; B.P. 136·8°/760 mm, n_D^{20} 1·4420 From data in the literature [10] the B.P. is 136·8/759 mm, n_D^{20} 1·4420.

Found %: H 11·33; C 68·50; Si 19·60

$C_8H_{16}Si$—calculated % H 11·50; C 68·48; Si 20·02

Polydimethyldiallylsilane

Found %: H 11·86; C 68·06; Si 20·15.

$(C_8H_{16}Si)_n$ Calculated %: H 11·50; C 68·48; Si 20·02

Methylphenyldiallylsilane was synthesized in a similar way from methylphenylchlorosilane; yield 37 per cent; B.P. 76·2°/1 mm, n_D^{20} 1·5218, d_4^{20} 0·9059, MR_D 68·09, MR_D (calc.) 68·04. Mol. wt.: found 207·0; calculated 202·3

Found %: H 9·07; C 77·31; Si 13·79.

$C_{13}H_{18}Si$ Calculated % H 8·97; C 77·11; Si 13·83.

Polymethylphenyldiallylsilane

Found %: H 9·23; C 77·22; Si 13·82.

$(C_{13}H_{18}Si)_n$ Calculated %: H 8·97; C 77·11; Si 13·83.

The polymerization was carried out in sealed ampoules in *n*-heptane purified from unsaturated compounds by drying and distilling over metallic sodium; solvent and monomers were distilled in a current of dry argon. The ampoules were evacuated to a residual pressure of 1–2 mm and filled then with dry argon; solvent, catalyst components and monomer from a Shank flask were then introduced. Polymerization was carried out with continuous shaking of the ampoule. At the end of an experiment the contents of the ampoule were poured into methyl alcohol, the polymer washed free from residual catalyst, dried at 40° under vacuum and extracted with benzene at room temperature. The characteristic viscosity of the soluble portion of the polymer was measured in benzene at 20° and the double bond content was determined by comparing the infrared spectra of the polymers and monomers on a fundamental frequency in the 906 cm^{-1} band and on the first overtone—in the 6110 cm^{-1} absorption band [11]

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SUMMARY

(1) Polymers of dimethyldiallylsilane and methylphenyldiallylsilane were obtained using a complex $Al(C_2H_5)_3-TiCl_4$ catalyst.

(2) The predominant polymer chain units are six-membered rings containing silicon which alternate with methylene groups.

Translated by R. G. P. TOWNDROW

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HETEROCHAIN POLYESTERS—XXIII. THE EFFECT OF THE STRUCTURE OF THE POLYESTER UNIT ON THE POLYESTER MELTING POINT*

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THE investigation and comparison of the properties of a large number of heterochain polyesters synthesised by us [1–26] indicated that the physical properties of polymers such, for example, as melting point, the temperature of transition into the visco-liquid state, solubility, the tendency toward crystallisation, tensile strength, elasticity etc., are connected with the structure of the polymer chain in the polyester and are determined in the main by three factors: the stereochemical regularity of the macromolecules, intermolecular forces and the flexibility of the polymer chain.

The melting point of a polyester, as in other crystalline polymers may be regarded as a measure of the stability of the crystalline structure. At this temperature the forces of interchain reaction in the molecules are in equilibrium with the thermal motion. In the general case the melting point is higher the less bending there is in the polymer chain and the greater the interchain reaction.

The molecular reaction of a polymer is determined by the cohesion energy of the structural groups in the macromolecule, i.e. it depends on the presence of polar groups in the macromolecule of the polymer, their concentration per unit length of chain and on their total number in the macromolecule. The interchain reaction also depends on the stereochemical regularity of the polymer chain which determines the density of packing of the polymer chains. Bunn [27] quotes more precise data on the value of the cohesion energy of various chemical groups and using them, calculates the cohesion energies per unit chain in certain polymer molecules relating them to the melting points of the polymers. Using Bunn's data on the values of the cohesion energies of various chemical groups it is of interest to consider the relationship of the melting points of the polymers with the average value of the cohesion energy per unit chain.

In fig. 1 is shown graphically the relationship of the change in melting point of aliphatic polyesters, polyesters of *p*-xylylene glycol, *m*-xylylene glycol, *p*-phenylenediacetic and diphenylmethane-4,4′-dicarboxylic acid (the second com-

* Vysokomol. soedin. **1**: No. 10, 1473–1481, 1959.

ponent from which the polyester was obtained being a polymethylene-dicarboxylic acid or a polymethylene glycol, respectively) as a relationship with the average cohesion energy per unit chain.

As seen in Fig. 1 the melting points of the polyesters of polymethylene-dicarboxylic acids and glycols in relation to the cohesion energy lie on two curves with minima which coincide with cohesion energy values of 900–1000 cal. Curve 1 corresponds to polyesters obtained from dicarboxylic acids and glycols with an even number of carbon atoms in the molecules; curve 2 refers to polyesters of dicarboxylic acids and glycols of which one has an odd number of carbon atoms per molecule. Thus for polyesters obtained from polymethylene-dicarboxylic acids and glycols containing only an even number of carbon atoms,

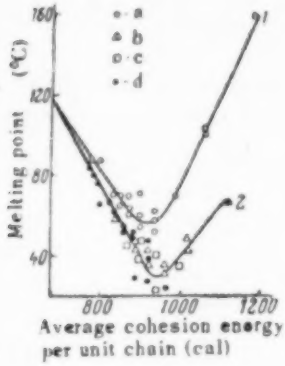

FIG. 1. Change in the melting point of polyesters of polymethylenedicarboxylic acids and glycols with the average cohesion energy per unit chain: (a) polyesters of dicarboxylic acids and glycols with even numbers of carbon atoms in their molecules; (b) polyesters of dicarboxylic acids with an even number of carbon atoms in the molecule and glycols with an odd number of carbon atoms in the molecule; (c) polyesters of dicarboxylic acids and glycols with odd numbers of carbon atoms in their molecules; (d) polyesters of dicarboxylic acids with an odd number of carbon atoms in the molecule and glycols with an even number of carbon atoms in the molecule.

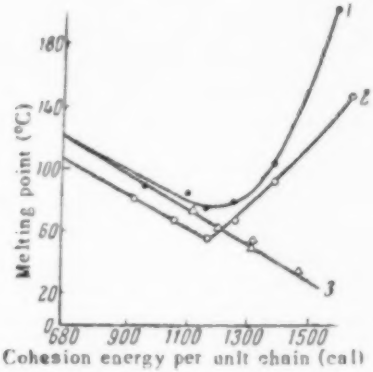

FIG. 2. Change in the melting point of polyesters with the average cohesion energy: (1) polyesters of *p*-xylylene glycol and polymethylenedicarboxylic acids with an even number of carbon atoms in their molecule; (2) polyesters of *p*-phenylenediacetic acid and polymethylene glycols with an even number of carbon atoms in their molecule; (3) polyesters of *p*-xylylene glycol and *p*-phenylenediacetic acid containing an uneven number of methylene groups in the recurring unit.

there is a higher melting point for the same value of cohesion energy than for those polyesters one of whose original components has an uneven number of carbon atoms.

At lower values for the magnitude of the cohesion energy, corresponding to the minimum melting points the curves approximate asymptotically to straight lines, which may be expressed by the following equations: M.P. $= -0{\cdot}36\varepsilon + 367$ and M.P. $= -0{\cdot}29\varepsilon + 323$ (for curves 1 and 2 respectively) where M.P. is the melting point of the polyester and ε is the average cohesion

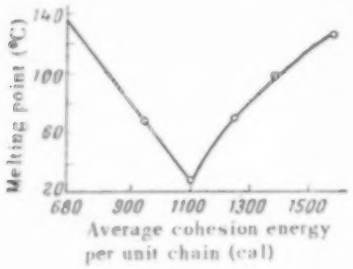

FIG. 3. Change in the melting point with average cohesion energy per unit chain of polyesters of *m*-xylylene glycol and polymethylenedicarboxylic acids with an even number of carbon atoms in the molecule.

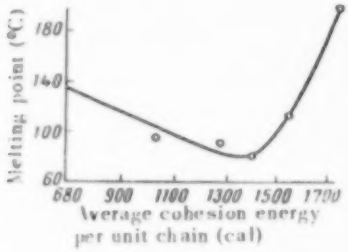

FIG. 4. Change in the melting point of polyesters of diphenylmethane-4,4′-dicarboxylic acid and polymethylene glycols with an even number of methylene groups in the molecule.

energy per unit chain. Thus, these straight lines intercept the ordinate axis at a point corresponding to the region of the melting point of polyethylene (cohesion energy at this point is 680 cal; according to the data of various authors the melting point of polyethylene is 104, 111, 124, 128, 133 and 136·5° [28–31]).

To the right of the minima also the curves appear to approximate asymptotically to straight lines, which correspond to the equations M.P. $= 0{\cdot}45\varepsilon - 382$ and M.P. $= 0{\cdot}24\varepsilon - 200$. From this it is seen that the slope of the line corresponding to the polyesters obtained from dicarboxylic acids and glycols with only an even number of carbon atoms in its molecule, is greater than in the case of polyesters of odd-type components. This implies that while the action of the evenness factor levels out and finally disappears with a decrease in the cohesion energy, the effect of the evenness factor increases with larger cohesion energies.

One would think that with an increase in the cohesion energy per unit chain, the melting point of the polymers of one or other of the homologous series would increase, because the high cohesion energy must also correspond to a stronger interchain reaction. The fact that in the series of aliphatic polyesters considered, the curves of melting point change with cohesion energy value pass through minima, indicates that it is not only the interchain reaction which specifies the magnitude of the melting point of a polyester.

It was noted by us above that the melting point of the polymer depends on the flexibility of the polymer chain. The effect on the polymer melting point of the flexibility of the polymer chain and the interchain reaction are in direct

contrast. In the homologous series of polyesters of polymethylenedicarboxylic acids and glycols two competing factors operate; the interchain reaction and the flexibility of the chain, the effect of which increases in proportion to a decrease in the number of methylene groups in the original components because this increases on one hand, the concentration of polar ester groups and on the other hand, the number of —O— bonds which increase the flexibility of the polymer chain. It may be concluded from Fig. 1 that in the homologous series of polyesters of polymethylenedicarboxylic acids and glycols the greatest chain flexiblity is possessed by polyesters whose average cohesion energy per unit chain is 900–1000 cal.

In Fig. 2 is presented graphically the relationship of the melting points of the polyesters of *p*-xylylene glycol and *p*-phenylenediacetic acid with the average cohesion energy per unit chain. It is seen from Fig. 2 that as a relationship with cohesion energy the melting point of the polyesters of *p*-xylylene glycol and *p*-phenylenediacetic acid containing an even number of methylene groups in the recurring units describes two linear curves with minima (as with aliphatic polyesters).

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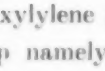
Curve 1 corresponds to the polyesters of *p*-xylylene glycol and curve 2 to the polyesters of *p*-phenylenediacetic acid. In relation to the cohesion energy the melting point of the *p*-xylylene glycol and *p*-phenylenediacetic acid polyesters containing an odd number of methylene groups in the recurring unit (with the exception of the polyester of *p*-phenylenediacetic acid and pentamethylene glycol) lies virtually on the straight line 3, which approximates asymptotically to curve 1 with a decrease in cohesion energy, and intercepts the ordinate axis with it at the point corresponding to the region of the melting point of polyethylene. Curve 2 is also a straight line to the left of the minimum intercepting the ordinate axis in the region of the melting point of polyethylene. Therefore the melting points of the *p*-xylylene glycol and *p*-phenylenediacetic acid polyesters converge to the melting point of polyethylene with a decrease in the number of methylene groups in the original components. The left-hand branches of curves 1 and 2 and the straight line 3 may be expressed by the following equations

$$1\text{: M.P.} = -0{\cdot}10\varepsilon + 190$$

$$2\text{: M.P.} = -0{\cdot}11\varepsilon + 179$$

$$3\text{: M.P.} = -0{\cdot}11\varepsilon + 197$$

The polyesters of *p*-xylylene glycol and *p*-phenylenediacetic acid are made up of one type of group namely from: $-CH_2-$,  , —CO— and —O—. Arising from this it may be anticipated that the same values of cohesion energy for the polyesters of *p*-xylylene glycol and *p*-phenylenediacetic acid should correspond to the same melting point i.e. their curve of melting point change against cohesion energy should be identical.

The fact that the *p*-phenylenediacetic acid polyesters possess a lower melting point at a certain cohesion energy than the polyesters of *p*-xylylene glycol is apparently connected either with less dense packing of the polymer chains in the *p*-phenylenediacetic acid polyesters, as a result of which the interchain reaction may not be fully realised, or with a greater flexibility of the polymer chain of the *p*-phenylenediacetic acid polyesters due to the spatial removal of the —O— bond from the aromatic nucleus.

In Fig. 5a a schematic representation is shown, as an example, of the polymer chains of the polyester of *p*-xylylene glycol with succinic acid and the polyester of *p*-phenylenediacetic acid with ethylene glycol.

In Fig. 3 the change in melting point of the polyesters of *m*-xylylene glycol with even-type polymethylenedicarboxylic acids is given as a relationship of the average cohesion energy per unit chain. As with the polyesters considered above the melting point change of *m*-xylylene glycol polyesters occurs on a curve with a minimum in relation to the average cohesion energy per unit chain; the minimum occurs at the cohesion energy value of 1100 cal. To the left of the minimum the graphical relationship is a straight line expressed by the equation: M.P. $= -0{\cdot}26\varepsilon + 310$ which intercepts the ordinate axis in the region of the melting point of polyethylene.

A comparison of the cohesion energy and the melting point of the *m*-xylylene glycol polyesters with the corresponding *p*-xylylene glycol polyesters indicates that at the same value of cohesion energy the *m*-xylylene glycol polyesters have lower melting points than the *p*-xylylene glycol polyesters. This demonstrates the presence of less dense packing in the polymer chains of *m*-xylylene glycol polyesters (see Fig. 5a) in comparison with *p*-xylylene glycol polyesters as a result of which there also occurs a weaker interchain reaction.

In the case of the polyesters of diphenylmethane-4,4′-dicarboxylic acid and glycols of general formula $HO(CH_2)_nOH$ where $n = 2, 4, 6, 10$ and 20 the melting point change also occurs on a curve with a minimum (see Fig. 4) as a relationship with the average cohesion energy per unit chain. To the left of the minimum the curve is a straight line, intercepting the ordinate axis in the region of the melting point of polyethylene and it may be expressed by the equation: M.P. $= -0{\cdot}09\varepsilon + 193$.

Generalising on the relationship considered above of the change in melting point of polyesters with the average cohesion energy per unit chain the following may be noted.

In the homologous series of polyesters with various structures synthesized by us there occurs a definite relationship between the melting point of the polyesters and the average cohesion energy per unit chain. An increase in the cohesion energy of polyesters containing an even number of methylene groups in their recurring unit does not cause a constant increase in the melting point of the polymer. The curves of melting point change of polyesters with cohesion energy pass through minima. In aliphatic polyesters this minimum occurs at

a cohesion energy value of 900–1000 cal; in the series of *p*-phenylenediacetic acid and *p*-xylylene glycol polyesters at a value of 1100–1200 cal; and in diphenylmethane-4,4′-dicarboxylic acid polyesters at 1300–1400 cal. Thus with the introduction into the chain of polyesters of the aromatic series and an increase in the number of aromatic nuclei a displacement of the minimum is observed in the range of the larger values of cohesion energy. The melting points of the polymers corresponding to the minima are also increased with an increase in the number of aromatic nuclei in the recurring unit from one to two.

To the left of the minimum there is a linear relationship between the change in melting point of polyesters with the value of the cohesion energy in which the slope of the straight lines is decreased with the introduction of an aromatic nucleus into the polymer chain and with an increase in the concentration of aromatic nuclei in the recurring unit.

The passage through minima of the curves of melting point change of polyesters against cohesion energy shows that the melting point depends not only on the interchain reaction but also on the flexibility of the polymer chain itself. The melting point of a polyester increases with an increase in the interchain reaction and decreases with an increase in the flexibility of the chain.

The fact that the change in melting point of polyesters of varying structure with the average cohesion energy per unit chain does not describe a common curve i.e. the same cohesion energy corresponding to an equal melting point, indicates that the interchain reaction depends strongly on the packing of the polymer chains. A less dense packing of the polymer chains does not produce the conditions for complete development of the interchain forces.

An investigation of many aliphatic polyesters [1–9] showed that the majority of crystalline aliphatic polyesters have melting points below 100°. Those polyesters existing in the amorphous state are heavy, viscous liquids. It could have been supposed that the introduction of an aromatic nucleus into an aliphatic polyester chain would increase its softening point.

The results obtained by us [10, 11, 16, 17] showed that the introduction of an aromatic or hydro-aromatic nucleus into the original components undoubtedly has an effect on the properties of the polyesters obtained by us. However the presence of an aromatic or hydro-aromatic nucleus in the recurring polyester unit is not in itself always sufficient to cause a substantial change in the properties of polyesters. In many polyesters of isomeric aromatic dicarboxylic acids [10, 11, 16] or diols [19, 21] it can be seen that the aromatic nucleus does not always "work".

It was noted by us above that the properties of polyesters are determined by the flexibility of the polymer chain and the magnitude of the interchain reaction. The polymer chains of aromatic polyesters are undoubtedly characterized by a lower flexibility than are the aliphatic polyesters since they contain an inflexible aromatic nucleus in their molecule. On the other hand the interchain reaction is also important, but in aromatic polyesters, sometimes, it does

not develop fully. For the realization of the interchain reaction good packing is important i.e. a high "packing factor" for the individual elements in the polymer molecules relative to each other, since it is known that the energy of the intermolecular forces of attraction decreases approximately proportionally to the sixth power of the distance between the molecules [32]. A low "packing factor" in certain polymer molecules of aromatic polyesters leads to the interchain reaction in which apparently no conclusive role is played, and to the interaction of π-electrons in the benzene rings of adjacent chains not developing fully.

The "packing factor" is closely connected with the structure of the original aromatic components, the mutual distribution of the various structural groups in it and the degree of symmetry of the original component. When its value is higher, then its chains are geometrically more densely packed and the greater the possibility of more complete development of the intermolecular interaction and, resulting from this, the higher the softening point of the polymer.

In Fig. 5b is shown, as an example, a schematic representation of the structure of polyesters of ethylene glycol with *tere*phthalic, *iso*phthalic and phthalic acids. From the Figure it is seen that the polyester of *tere*phthalic acid should have the highest "packing factor" (due to the greater symmetry of its molecule) and phthalic acid should have the lowest.

The aromatic nucleus in *iso*phthalic acid, and particularly *ortho*phthalic acid, plays the part of a wedge separating the polymer chains and preventing the establishment of denser packing in the polymer chains.

The extra rigidity of the polymer chain due to the aromatic nucleus in similar cases is sometimes insufficient to compensate for the incomplete development of the interchain reaction due to this spacing. The latter may also be seen clearly by comparing, for example, the polyesters of sebacic acid with pentamethylene glycol and *m*-xylylene glycol (see Fig. 5b). The polyester of *m*-xylylene glycol contains inflexible parts (aromatic nuclei) in its chain and its average cohesion energy per unit chain is equal to 1100 cal. The average cohesion energy per unit chain in polypentamethylene sebacate is only 860 cal, but nevertheless, the pentamethylene glycol polyester has a higher softening point (53°) than the *m*-xylene glycol polyester (27°). A higher softening point for the polyester of pentamethylene glycol will be apparent if we compare the structure of the polymer chains of these two polyesters, presented in Fig. 5b. It is seen from Fig. 5b that the "packing factor" in the polyester of *m*-xylylene glycol should have a lower value than the polyester of pentamethylene glycol. As a result of this the interchain reaction cannot be realized to such an extent as would have been expected from the cohesion energy and this also is reflected in the properties which condition the interchain reaction.

Thus, from the point of view of obtaining polyesters with the highest softening point it is important not merely to have aromatic nuclei in the polymer chain but a combination of two factors; a high flexibility of the polymer chain due

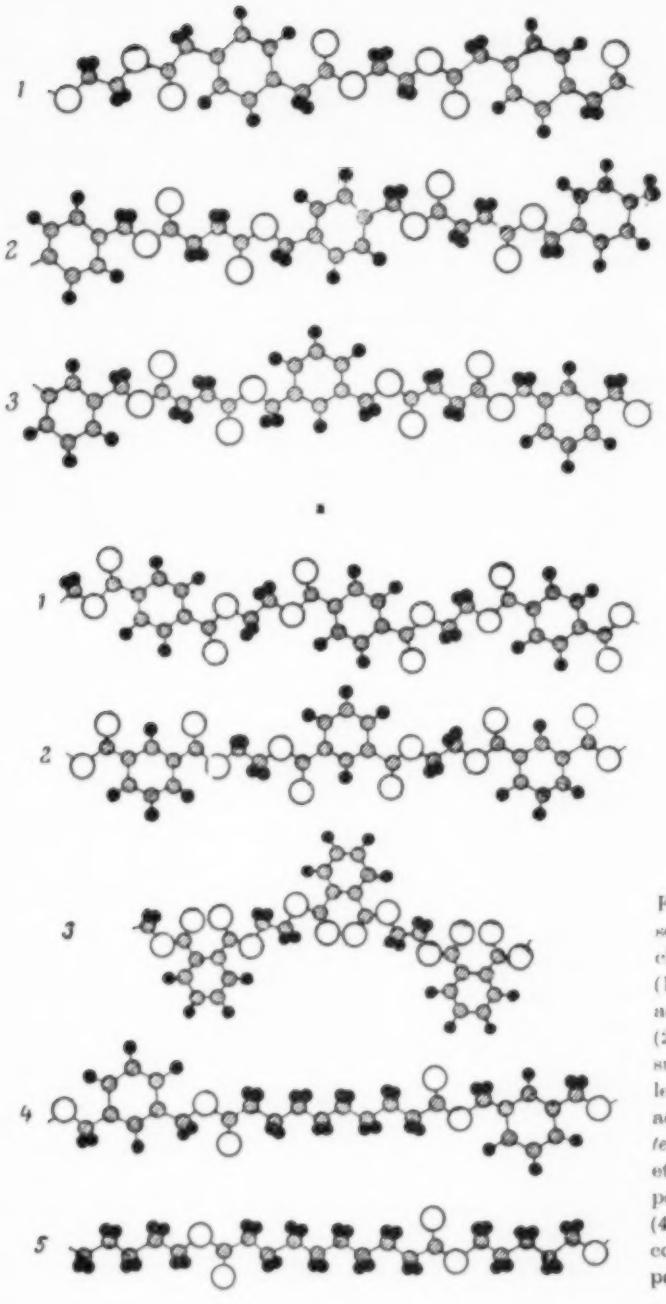


FIG. 5. Schematic representation of the polymer chains of polyesters: (a) (1) *p*-phenylene diacetic acid with ethylene glycol; (2) *p*-xylylene glycol with succinic acid; (3) *m*- xylylene glycol with succinic acid. (b) (1) polyethylene *tere*phthalate; (2) polyethylene *iso*phthalate; (3) polyethylene phthalate; (4) poly-(*m*-xylylene glycol) succinate; (5) polypentamethylene succinate.

to aromatic units and a high value for the "packing factor" ensuring the possibility of the complete utilisation of the intermolecular forces.

The magnitude of the "packing factor" also has a great effect on the ability of polyesters to crystallise. As a rule the aromatic polyesters with flexible macromolecules having a high value for the "packing factor" are crystalline materials (for example polyhydroxyquinone *tere*phthalate) and conversely in aromatic polyesters with a low value for the "packing factor" the ability to crystallize is greatly decreased (for example, the polyesters of *iso*phthalic and diphenyl-3,3-dicarboxylic acids, the polyesters of *p,p'*-dioxydiphenylpropane, etc.).

SUMMARY

(1) The relationship of the melting point of a polyester with its average cohesion energy per unit chain and the density of packing of the polymer chains is established using heterogeneous complex polyesters of different structures as examples.

(2) It is shown that the melting point of a polyester is determined by the degree of intermolecular interaction and the flexibility of the polymer chain.

Translated by R. G. P. TOWNDROW

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CARBOCHAIN POLYMERS AND COPOLYMERS—XVII. POLYMERIZATION OF DIALLYL DERIVATIVES OF SILICON AND GERMANIUM*

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FOR some time past it has been found that polymers possessing high thermal stability, the ability to form films and which are soluble in organic solvents may be obtained from compounds containing isolated double bonds. 1,6-heptadiene, 1,5-hexadiene, 2,5-dimethyl-1,5-hexadiene [1] α,α'-dimethylenepimelic acid and its esters [2], diallyldiethylammonium bromide [3] are included in the number of such compounds. The polymerization of these compounds occurs either in the presence of initiators [2,3] or by the action of complex metal-alkyl catalysts [1]; as a result of polymerization polymers are formed which contain five-or six-membered rings in the primary chain [3].

We attempted to extend the cyclic polymerization reaction to diallyl derivatives of silicon and germanium which may be considered as structural analogues of a 4,4-dialkyl-1,6-heptadiene. With this aim we synthesized diallyldimethylsilane (B.P. 136–137°, n_D^{20} 1·4420; literature data B.P. 136·8°, n_D^{20} 1·4420 [4]) diallyldiethylsilane (B.P. 79–80°/20 mm, n_D^{20} 1·4595; literature data B.P. 91°/34 mm, n_D^{20} 1·4594 [4]) and diallyldimethyl germane (B.P. 146–147°, n_D^{20} 1·4640; literature data B.P. 146°, n_D^{20} 1·4645 [5]). The attempt at polymerizing these monomers in the presence of 2 per cent by weight of benzoyl peroxide at 60°, in twice the quantity of benzene over the course of 50 hr in a current of nitrogen proved to be unsuccessful and no polymer was obtained. These results agree with the data of Korshak and co-workers [6] who showed that diallyldialkylsilanes and germanes do not polymerize in the presence of peroxide initiators at atmospheric pressure.

The polymerization of diallyldiethylsilane and diallyl and diallyldimethylgermane in the conditions described by Marvel and Stille [1] was more successful. We took 2·5 moles per cent triethyl aluminium, 2·5 moles per cent titanium tetrachloride and 2–3 times the amount of benzine-solution (B.P. 90–100°) (all on the basis of a given quantity of monomer); we carried out the polymerization over the course of 8 hr at 60° in a current of nitrogen. We decomposed the reaction mixture with methyl alcohol and acidified water, separated

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the organic layer and distilled off the solvent at a pressure of 40–50 mm and a temperature not higher than 50°. We dissolved the residue in the benzine-solution and precipitated the polymer with butanone.

As a result of the polymerization of diallyldiethylsilane a viscous slightly-coloured polymer was obtained in a yield of about 10 per cent. The molecular weight of the polymer determined by the ebullioscopic method (in dioxane) was shown to be 650° which is close to the molecular weight of the tetramer (673·2). The silicon content of the polymer was 16·30 and 16·12 per cent which agrees well with the silicon content in the diallyldiethylsilane tetramer, 16·68 per cent. A comparison of the IR spectra of monomeric diallyldiethylsilane

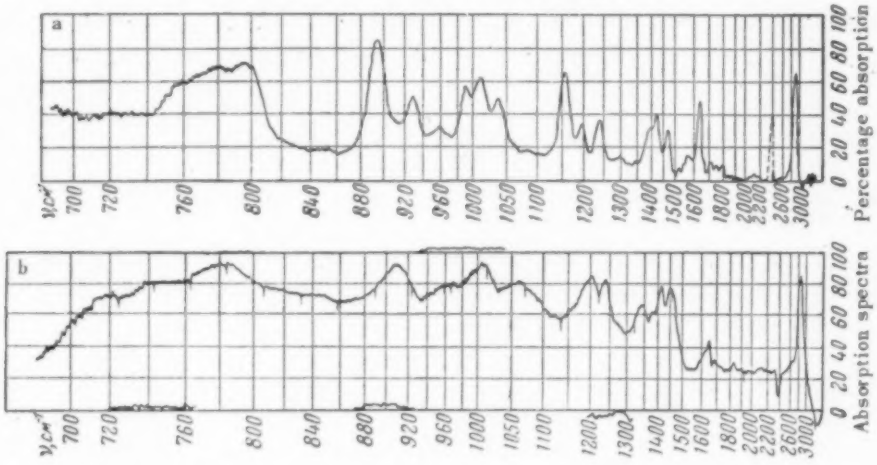
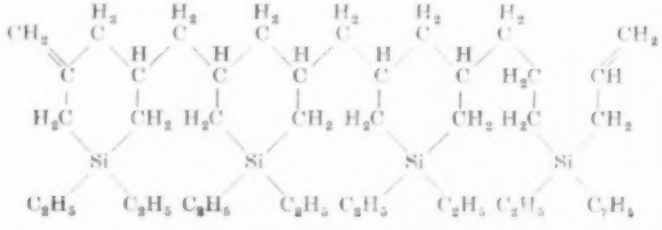


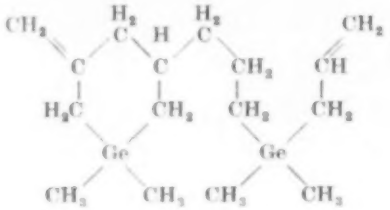
FIG. 1. Absorption spectra. (a) Diallyldiethylsilane; (b) Diallyldiethylsilane tetramer.

and the tetramer produced (Fig. 1a and b) indicates a sharp reduction in unsaturation (by approximately 4 times) (absorption band at 1630–1650 cm^{-1}). A comparison of these spectra also shows that a considerable change in the structure of the molecule occurred as a result of polymerization, possibly connected with the formation of the ring-containing tetramer to which, for example, may be ascribed the structure.



Such a tetramer contains two double bonds, i.e. 4 times less than the double bonds contained in four molecules of diallyldiethylsilane.

As a result of the polymerization of diallyldimethylgermane in the conditions described above a coloured oil was obtained in a yield of about 50 per cent. The molecular weight was found to equal 270 (ebullioscopically in dichloroethane) which is below the molecular weight of the dimer of diallyldimethylgermane (365·6). A comparison of the IR-spectra of diallyldimethylgermane and the polymerization product indicated comparatively little reduction in unsaturation (approximately twice) and insignificant change in the structure of the molecule. The principal polymerization product in this case is apparently the dimer and may have the cyclic structure



The cyclic dimer also differs from the structure of monomeric diallyldimethylgermane but to a lesser degree than the diallyldiethylsilane tetramer differs from monomeric diallyldiethylsilane.

An increase in the concentration of catalyst up to 4 per cent leads to a lowering of the yield of products from the polymerization of diethyldiallylsilane and diallyldimethylgermane.

Attempts at carrying out the polymerization of diallyldimethylsilane, diallyldiethylsilane and diallyldimethylgermane in the presence of boron fluoride, tributyl boron or mixtures of these materials proved to be unsuccessful. On copolymerizing the monomers indicated with ethylene in the presence of a mixture of triethyl aluminium and titanium tetrachloride, only polyethylene was obtained.

The authors offer sincere gratitude to S. A. Pavlova for the determination of the molecular weights, N. A. Chumayevskii for recording the spectra and E. M. Popov for help in discussing the results of the spectral analyses.

SUMMARY

It is shown that diallyl derivatives of silicon and germanium form polymers of low molecular weight in the presence of a mixture of triethyl aluminium and titanium tetrachloride. Suggestions are expressed on the structure of the polymerization products.

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POLYDIMETHYLGERMANASILOXANES*

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MODERN technology requires the manufacture of polymer substances akin to rubber and with a high level of resistance to thermal action. Polyorganosiloxane rubbers which are workable at temperatures from −50 to +250°C are being consumed to an increasing extent relative to the semi-organic polymers. The presence of Si—O bonds which form the skeleton of the molecule, and the presence of organic radicals attached to the silicon atoms, place the organosilicon rubbers in a position intermediate between the inorganic and the organic polymers.

In recent years successful attempts have been made to synthesize polymer compounds containing a grouping of the type Si—O—E—O—Si—O— and Si—O—E—O—E′—O—. This new class of polymers constitutes a link between the organosilicon polymers—polysiloxanes, and silicates [1,2]. It is pointed out in the literature that the insertion of atoms of other metals into the siloxane structure enhances the resistance of the polymers to thermal action. However the literature has contained as yet no reference to rubber-like polyorganometallasiloxanes. Polyorganogermanasiloxanes† were likewise unknown although monomers containing Si—O—Ge bonds were recently prepared [3].

It was important to study the partial replacement of the silicon atoms in the polysiloxane structure by germanium atoms and examine their influence on the properties of siloxane polymers.

EXPERIMENTAL

With a view to obtaining germanasiloxane polymers, experiments were conducted on the joint hydrolysis of dimethyldichlorosilane with dimethyldichloro(bromo) germanium. Rectified dimethyldichlorosilane (DDS) from which polydimethylsiloxane rubber (DSR) is prepared, was used for these experiments.

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† In accordance with the "oxa-aza" concept of organosilicon nomenclature the prefix "germana" indicates the replacement of silicon atoms by germanium atoms.

The synthesis and properties of dimethyldichlorogermanium (DCG) and dimethyldibromogermanium (DBG) have previously been reported by two of us [4].

In the control hydrolysis of DBG with water in the ratio of 2:1 by weight, a two-phase system was formed. The liquid bottom phase, a hydrolysis product, dissolved in an excess of water. Neutralization of the solution (rendered acid by the liberation of HBr on hydrolysis) with potash produced a solid phase, i.e. a white, insoluble substance corresponding in composition to the formula $(CH_3)_2GeO$. This accords with the literature in respect of the intermediate formation of dialkylgermanodiols on hydrolysis of compounds of the type R_2GeX_2 [5]

$$(CH_3)_2GeBr_2 + 2H_2O \xrightarrow{-HBr} (CH_3)_2Ge(OH)_2 \xrightarrow{-H_2O} [(CH_3)_2GeO]_n.$$

The hydrolysis of a mixture of DDS with DBG in a molar ratio of 95:5 yielded colourless, oily products. The presence of germanium in the polymer was established qualitatively by analysis of the emission spectrum. Ultimate-analysis of the neutral, desiccated polymer indicated that it contained $(CH_3)_2SiO$ and $(CH_3)_2GeO$ segments in the ratio of 98:2.

In the following experiments on the joint hydrolysis of dimethyldichlorosilane with dimethyldihalidogermanium compounds the hydrolizing medium used was a mixture of alcohol and water. With brisk stirring the monomer mixture was introduced at a rate of 0·8–0,9 mol/hr into a flask containing the water-alcohol mixture cooled to 5–10°C and in a volumetric ratio of 2·2–2·4:1 with respect to the monomer mixture. The ultimate acidity of the water-alcohol phase was 23–25 per cent by weight. The organic phase was separated from the acid by washing with water and dried over calcined potash, after which the resulting products were analysed and their constants determined *. The results given in Table 1 show that the cohydrolysis of dimethyldichlorosilane and dimethyldihalidogermanium compounds in a water-alcohol medium yields oily low molecular polydimethylgermanasiloxanes with a mainly cyclic structure. It should be noted that with an initial molar ratio $(CH_3)_2SiCl_2 : (CH_3)_2GeX_2 = 95:5$ the conditions of hydrolysis determine just the physico-chemical characteristics which depend upon the molecular weight of the product but do not affect its composition.

With a view to preparing rubber-like polymers the low molecular germanasiloxanes synthesized by us for the first time were polymerized by a method developed at the All-Union Scientific Research Institute for Rubber (VNIISK) for cyclic polydimethylsiloxanes, viz. by mixing a siloxane oil with conc. H_2SO_4 and then diluting the acid with water [6].

* Analysis of the emission spectra was performed by Zil'bershtein at the Institute of Silicate Chemistry of the U.S.S.R. Academy of Sciences. The ultimate-analysis was carried out in the Laboratory for Organic Microanalysis of the Institute of Organic Chemistry of the U.S.S.R. Academy of Sciences.

Polymerization of the oil from experiment 3 (Table 1) yielded a viscous, liquid polymer. In all other cases we obtained soft, non-viscous rubber-like products of high molecular weight similar to polydimethylsiloxane rubber DSR but containing atoms of germanium in the siloxane structure (Table 2).

It can be seen from the results listed in Table 2 that the polymerization of germanasiloxane oils proceeds more slowly than that of normal cyclic dimethylsiloxanes. Some time after the introduction of the conc. H_2SO_4 the system forms two phases by the flocculating out of a white precipitate. Continued stirring is attended by the disappearance of the second phase, the oil gradually thickens and after dilution of the acid with water is converted to a homogeneous, transparent linear polymer akin to rubber. Evidently under the action of the H_2SO_4 on the low molecular dimethylgermanasiloxanes scission of the Ge—O—Si bonds takes place first of all with the intermediate separation of dimethylgermoxane fragments which then enter into reaction with the dimethylsiloxane segments of the chain to form high molecular germanasiloxanes *. In this way it was possible for the first time to prepare rubber-like polyorganometallasiloxanes.

The molecular weight of reference samples of polydimethylsiloxane rubber was determined by a simplified method developed at the VNIISK. Two samples were taken from a 0·025 M solution of the rubber in benzene (the weight of a single dimethylsiloxane segment was assumed to be 1 mol) and a parallel determination carried out (Ostwald capillary viscometer) of the reduced viscosity which can be taken as a characteristic. Furthermore use was made of the formula derived by Barry [7] for polydimethylsiloxanes $[\eta]=KM^{0.66}$ where K in the present case is equal to $1{\cdot}5\times10^{-3}$.

The molecular weights listed in Table 2 for polydimethylgermanasiloxane rubbers are appraisable for the reason that the experimental values found for the intrinsic viscosity (determined by repeatedly diluting samples of a solution composed of 1 g rubber in 100 ml benzene) were substituted in the form of Barry's formula specifically adapted for high molecular polydimethylsiloxanes by Korolev and co-workers [8], viz. $[\eta]=2{\cdot}15\times10^{-4}\times M^{0.66}$ †. Unfortunately the validity of this formula for new forms of siloxane rubber has not yet been established although in calculating the molecular weight of dimethylsiloxane rubbers containing up to 4 mol.% $(CH_3)(CH_2{=}CH)SiO$ segments Polmanteer and Koch [9] used Barry's original formula $[\eta]=2\times10^{-4}M^{0.66}$. Recently [10] Andrianov and Iakushkina applied Korolev's formula to calculate the molecular weight of methylphenylsiloxane copolymers.

* The polydimethylgermanasiloxane obtained by us (experiment 8, Table 1) is insoluble in the siloxane oil.

† Recently [10] Andrianov and Iakushkina applied Korolev's formula to calculate the molecular weight of methylphenylsiloxane copolymers.

TABLE 1. COHYDROLYSIS OF DIMETHYLDICHLOROSILANE WITH DIMETHYLDIHALIDOGERMANES IN A WATER–ALCOHOL MEDIUM

No. of expt.	Starting $(CH_3)_2GeX_2$	Used for hydrolysis (mols)		Yield of dry hydrolysis product (g)	Properties of hydrolysate						Ultimate analysis			
									OH – groups (%)		found (%)			Composition of copolymer calculated from analysis results
		$(CH_3)_2SiCl_2$	$(CH_3)_2GeX_2$		n_D^{20}	d_4^{20}	η^{20} (centi poises)	Mol. wt.†	found	calculated from mol. wt.	C	H	Si + Ge	
1	–	1·55	–	93·7	1·3982	0·9582	3·45	352	0·06	9·66	–	–	–	polydimethylsiloxane
2	X = Cl	2·425	0·075	168·0	1·3987	0·9603	4·14	369	–	–	–	–	–	polydimethyl-germanasiloxane‡
3	X = Br*	1·425	0·075	79·5	1·4034	0·9797	–	582	0·16	5·84	32·03	8·03	38·61	$(CH_3)_2SiO_{93}(CH_3)_2GeO_6$
4	X = Br	1·539	0·081	83·5	1·3986	0·9607	–	357	0·03	9·52	32·01	8·05	38·61	$(CH_3)_2SiO_{93}(CH_3)_2GeO_6$
5	X = Cl	2·38	0·125	169·0	1·3989	0·9607	4·04	356	–	–	–	–	–	polydimethyl-germanasiloxane‡
6	Ditto	1·35	0·15	83·5	1·3987	0·9597	–	357	0·03	9·52	31·61	7·93	39·39	$(CH_3)_2SiO_{96}(CH_3)_2GeO_4$
7	,, ,,	0·65	0·1625	43·0	1·4004	0·9665	4·46	416	–	–	–	7·78	–	$(CH_3)_2SiO_{92}(CH_3)_2GeO_8$
8	X = Br*	–	0·0425	–	solid insoluble polymer						20·27	5·00	61·25	$(CH_3)_2GeO$

* Hydrolysis carried out with water. † Determined cryoscopically in benzene. ‡ Analysis of the emission spectrum confirmed the presence of Ge in the copolymer.

TABLE 2. POLYMERIZATION OF LOW MOLECULAR GERMANASILOXANES

Hydrolysis product of expt. No.	Ge content in hydrolysis product (%)	Polymerization conditions		Yield of dry neutral polymer (%)	Polymer properties					Polymer
		H_2SO_4 (% wt.)	Mixing time prior to dilution of acid (hr)		Intrinsic viscosity [η]	Mol. wt x 10^{-3}	Content of volatile substances (4 hr at 150°C) (wt. %)	Solubility in benzene (%)	Glass transition temperature (°C)	
1	–	2	6	91·0	8·59	494·0	6·9	100	–123	DMS
2	+	4	6	89·1	0·880	360·4	3·6	100	–124	GS-2
4	1·93	4	4	86·4	1·403	738·9	5·9	100	not determined	GS-4
5	+	4	6·3	85·8	1·500	818·9	1·9	100	–123	GS-4
6	3·82	4	6·5	86·2	0·997	437·0	3·3	100	–122	GS-6
7	7·48	6	10·5	88·0	1·007	443·6	3·8	98	–121	GS-7

TABLE 3. PROPERTIES OF THE VULCANIZATES

Starting rubber*	Properties									
	Before heat treatment†				After heating at 250°C for:					
					75 hr			120 hr		
	Tensile strength (kg/cm²)	Relative elongation (%)	Swelling after 3 days, (%)		Tensile strength (kg/cm²)	Specific elongation (%)	Heat stability coefficient ‡	Tensile strength (kg/cm²)	Specific elongation (%)	Heat stability coefficient
			in benzine	in benzene						
SKT	41	285	169	139	36	110	0·39	38	85	0·30
DMS	35	265	172	139	39	85	0·32	—	—	—
GS-2	37	240	165	134	37	95	0·40	41	75	0·31
GS-4	34	230	148	117	44	100	0·46	40	75	0·33
GS-5	38	210	162	132	36	90	0·43	33	65	0·31
GS-6	37	230	150	123	—	—	—	—	—	—
GS-7	34	185	145	114	—	—	—	36	45	0·24

* Cf. table 2. † Composition of mixtures (parts by wt): polymer – 100; powdered silica gel U-333-50; zinc. oxide – 5; benzoyl peroxide – 2; vulcanization – 10 min at 120°C in a press and 6 hr at 200°C in a thermostat. ‡ From the specific elongation. § For DSR – after 360 hr. †† Prehardening – 6 hr at 250°C. ‡‡ For DSR – after 72 hr.

On the basis of the polydimethylgermanasiloxane rubbers synthesized by us, vulcanizates were prepared of which the properties are set out in Table 3. This Table shows that the specific elongation of the vulcanizates falls inversely with germanium content in the polymer. At the same time with their ability to withstand temperatures of 250–300°C the germanasiloxane vulcanizates are not inferior to standard DSR and a number of them are better than laboratory specimens based on a rubber prepared from a non-dispersed hydrolysate of DDS.

Thus the incorporation of germanium atoms in a siloxane structure produces no substantial change in the properties of siloxane polymers and, in particular, does not enhance the thermal stability of polysiloxane rubber vulcanizates.

CONCLUSIONS

(1) The incorporation of germanium atoms in a siloxane structure is shown to be possible by the joint hydrolysis of dimethylchlorosilane with dimethyldihalidogermanes. Low molecular cyclic polydimethylgermanasiloxanes are obtained for the first time.

(2) High molecular, rubber-like polydimethylgermanasiloxanes are prepared and constitute the first examples of the polyorganometallasiloxane class of elastomers. It is established that the properties of the prepared polymers and of their vulcanizates are analogous to those of DSR rubber and vulcanizates.

Translated by G. CAMERON

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OF GERMANASILOXANE RUBBERS

of vulcanizates †

240 hr§			24 hr ‡‡			48 hr‖		
Tensile strength (kg/cm²)	Specific elongation (%)	Heat stability coefficient	Tensile strength (kg/cm²)	Specific elongation (%)	Heat stability coefficient	Tensile strength (kg/cm²)	Specific elongation (%)	Heat stability coefficient
43	65	0·23	28	80	0·28	31	30	0·10
—	—	—	—	—	—	—	—	—
40	40	0·17	32	65	0·27	34	50	0·21
—	—	—	—	—	—	—	—	—
33	50	0·24	30	55	0·26	28	55	0·25
—	—	—	28	55	0·24	—	—	—
—	—	—	—	—	—	—	—	—

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ORGANO-TIN MONOMERS AND POLYMERS*

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THE possibility of polymerization and copolymerization of organo-tin trialkyl stannyl methacrylates and dialkylstannylene dimethacrylates was established by us earlier [1, 2]. In the present communication, syntheses of trialkyl(aryl) stannyl methacrylates $R_3SnOCOC(CH_3)=CH_2$ and of dialkyl(aryl)stannylene dimethacrylates $R_2Sn[OCOC(CH_3)=CH_2]_2$, where R is from CH_3 to C_8H_{17} and C_6H_5 are described; it is established that the indicated compounds polymerize and copolymerize with unsaturated compounds—methyl methacrylate, styrene, *cyclo*pentadiene, and other monomers.

Together with the compounds mentioned, we obtained trimethyl- and triphenylstannols and also hexa-alkyl(aryl)stannoxides $R_3SnOSnR_3$: hexapropyl-, hexabutyl-, hexa*iso*butyl-, hexa*iso*amyl-, hexahexyl-, hexaheptyl-, and hexaoctylstannoxides. The hexa-alkylstannoxides listed were synthesized first. Some physico-chemical properties of the hexa-alkyl(aryl)stannoxides synthesized are given in Table 1.

Trimethyl- and triethylstannols form white pulverulent substances soluble in water and ether and insoluble in petroleum ether and chloroform. Tripropyl-, tributyl- and tri-*iso*butyl and the higher hydroxy compounds are unstable compounds and readily undergo dehydration with the formation of the corresponding hexa-alkyl(aryl)stannoxides $R_3SnOSnR_3$. The production of tributylstannol itself, as indicated in a recently published communication [3], is doubtful. By repeated syntheses, elementary analyses and molecular weight determinations, in benzene and dioxan we established that the product of the hydrolysis of $(n\text{-}C_4H_9)_3SnX$ is hexabutylstannoxide $(n\text{-}C_4H_9)_3SnOSn(n\text{-}C_4H_9)_3$, and not tributylstannol $(n\text{-}C_4H_9)_3SnOH$ as Koton assumed [3]. We observed similar transformations in the case of the hydrolysis of tripropyl-, tri-*iso*butyl-, triamyl-, trihexyl-, triheptyl-, and trioctylbromostannanes. The results of the analyses are given in Table 1.

Hexa-alkyl stannoxides are liquids soluble in the usual organic solvents. Hexamethylstannoxide was not obtained in pure form but the other members

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TABLE 1. PHYSICO-CHEMICAL PROPERTIES OF HEXA-ALKYL (ARYL) STANNOXIDES

Formula	b.p., °C (mm)	n_D^{20}	d_4^{20}	Yield (% of theory)	MR_D		Analysis, %						Mol. wt	
							C		H		Sn		found by the cryoscopic method	calc.
					Calc.	found	found	calc.	found	calc.	found	calc.		
$(C_2H_5)_3SnOSn(C_2H_5)_3$	156–158(28)	14,965	13,774		90·84	90·73	42·14	42·23	7·95	8·26	46·89	46·37	495·5 in dioxan	511·92
$(n\text{-}C_3H_7)_3SnOSn(n\text{-}C_3H_7)_3$	148(3)	14,915	12,514		118·62	118·07	42·38		7·97		45·68			
$(n\text{-}C_4H_9)_3SnOSn(n\text{-}C_4H_9)_3$	186,5–187(3)	14,862	11,715	30·0	146·36	146·40	47·79 47·82	48·35	9·06 8·99	9·13	40·32 40·01	39·82	533·90 in benzene	596·07
$(iso\text{-}C_4H_9)_3SnOSn(iso\text{-}C_4H_9)_3$	165,3(3)	14,860	11,744	28·0	146·0	145·72	48·23 48·40	48·35	9·00 8·97	9·13	40·49 40·03	39·82	550·4 502·2 in benzene	596·07
$(iso\text{-}C_5H_{11})_3SnOSn(iso\text{-}C_5H_{11})_3$	188(2)	14,803	11,067	31·0	174·2	174·6							408·9 in benzene	416
$(n\text{-}C_6H_{13})_3SnOSn(n\text{-}C_6H_{13})_3$	248–250(2)	14,820	10,888	29·5	201·96	201·01	59·90 59·71	59·44	10·74 10·81	10·69	27·94 28·13	27·97	665·1 in benzene	708
$(n\text{-}C_7H_{15})_3SnOSn(n\text{-}C_7H_{15})_3$	277–278(2)	14,802	10,506	26·3	229·6	230								

were readily prepared; they are stable compounds and distill in vacuum without decomposition. Hexaethylstannoxide reacts with water with the formation of triethylstannol:

$$(C_2H_5)_3SnOSn(C_2H_5)_3 + H_2O \rightarrow 2(C_2H_5)_3SnOH$$

The higher hexa-alkylstannoxides do not react with water. We found that in the hydrolysis of trialkyl(aryl)halogenostannanes with aqueous alkali solutions a disproportionation reaction may be observed. Thus, in place of the expected trialkyl(aryl)stannols, dialkyl(aryl)stannones, hexa-alkyl(aryl)stannoxides and tetra-alkyl(aryl)stannanes are formed:

$$4R_4SnX + 4KOH \rightarrow R_3SnOSnR_3 + R_4Sn + R_2SnO + 4KX + H_2O.$$

This reaction may be a method of obtaining the dialkyl(aryl)stannones R_2SnO and the hexa-alkyl(aryl)stannoxides $R_3SnOSnR_3$.

The dialkyl(aryl)stannones are white amorphous substances which are insoluble in water and organic solvents. The dialkyl(aryl)stannones and the hexa-alkyl(aryl)stannoxides are extremely reactive substances. They readily react with unsaturated acids, for example, methacrylic, with the formation of the corresponding organo-tin methacrylates.

Anderson [4], studying the reaction of hexaethylstannoxide with a series of organic acids, thought that methacrylic acid would polymerize under the conditions of the reaction with hexaethylstannoxide, but did not test this supposition by experiment. We established that the reaction indicated proceeds very readily and that various trialkylstannyl methacrylates are formed in it according to the hexa-alkylstannoxides taken for the reaction. Some properties of the organo-tin methacrylates obtained are indicated in Table 2.

It was also established that trialkyl(aryl)stannols and dialkyl(aryl)stannones also react with methacrylic acid to form the corresponding trialkyl(aryl)stannyl methacrylates and dialkyl(aryl)stannylene dimethacrylates.

The organo-tin mono- and dimethacrylates readily polymerize and copolymerize with unsaturated monomers. The properties of the organo-tin polymers and the copolymers with methyl methacrylate are shown in Table 3. The thermomechanical properties of the polymers and copolymers obtained are given in the graphs (a and b).

It can be seen from the graphs that the copolymers of dibutylstannylene dimethacrylate and diethylstannylene dimethacrylate with methyl methacrylate possess a region of high deformation above 200°.

Polymers of the trialkylstannyl methacrylates, for example, triethylstannyl methacrylate, exhibit a high adhesion to glass and metal.

The polymerization and copolymerization of trimethyl-, triethyl-, tripropyl-, and tributylstannyl methacrylates, and also of the dialkylstannylene dimethacrylates containing the same alkyl radicals, was carried out by us by the bulk method in the presence of an initiator of the radical type at temperatures from 60 to 160° (depending on the radical) for 24 hr.

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TABLE 2. PHYSICO-CHEMICAL PROPERTIES OF TRIALKYL (ARYL) STANNYL METHACRYLATES $R_3SnOCOC(CH_3)=CH_2$ AND DIALKYL (ARYL STANNYLENE DIMETHACRYLATES $R_2Sn[OCOC(CH_3)=CH_2]_2$

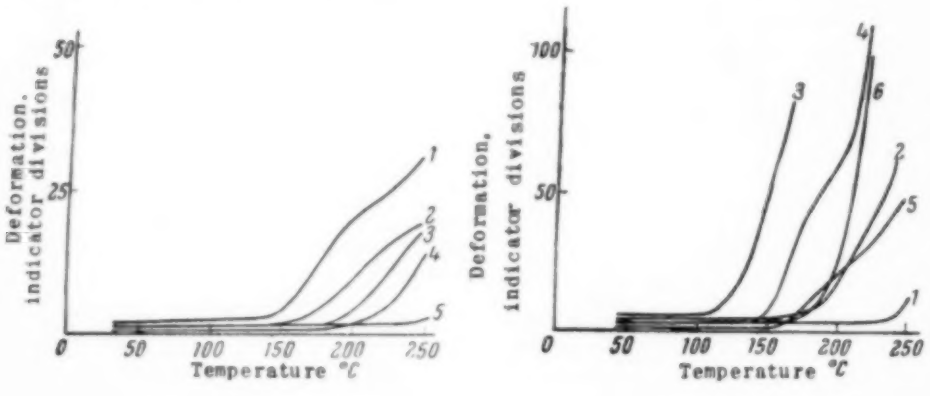
Formula (MA = OCOC(CH₃)=CH₂)	m.p. °C	n_D^{20}	d_4^{20}	MR_D		Yield, (% of theory)	Analysis, %			
							C		H	
				calc.	found		calc.	found	calc.	found
$(CH_3)_3SnMA$[2]	110	—	—	—	—	72·1	33·90	33·78	5·60	5·66
							33·94		5·52	
$(C_2H_5)_3SnMA$	75·0	—	—	—	—	81·0				
$(n\text{-}C_3H_7)_3SnMA$[1]	48·5	—	—	—	—	83·0	47·03	46·86	8·07	7·88
							46·81		7·82	
$(n\text{-}C_4H_9)_3SnMA$[1]	17·0	14,805	15,651	92·87	92·23	78·0				
$(iso\text{-}C_4H_9)_3SnMA$[1]	10·0	14,804	15,649	92·87	92·20	80·0				
$(iso\text{-}C_5H_{11})_3SnMA$[1]	15·0	14,790	10,999	107·1	107·5	78·5				
$(n\text{-}C_6H_{13})_3SnMA$[1]	19·0	14,820	10,688	120·2	120·2	79·0				
$(n\text{-}C_7H_{15})_3SnMA$[1]	23·0	14,844*	10,599*	134·9	135·4	77·0				
$(C_6H_5)_3SnMA$[3]	86·0	—	—	—	—	65·6				
$(CH_3)_2Sn(MA)^2_2$	141·0	—	—	—	—	70·6				
$(C_2H_5)_2Sn(MA)^1_2$	137·0	—	—	—	—	79·9				
$(n\text{-}C_3H_7)_2Sn(MA)^1_2$	61·0	—	—	—	—	81·0	45·44	44·86	6·69	6·48
							45·54		6·63	
$(n\text{-}C_4H_9)_2Sn(MA)^1_2$	50·0	—	—	—	—	85·0				
$(iso\text{-}C_4H_9)_2Sn(MA)^1_2$	36·0	—	—	—	—	82·0				
$(iso\text{-}C_5H_{11})_2Sn(MA)^1_2$	75·0	—	—	—	—	83·0				
$(n\text{-}C_7H_{15})_2Sn(MA)^1_2$	21·0	—	—	—	—	76·7	54·92	54·26	7·82	8·2
							54·78		7·96	
$(n\text{-}C_6H_{13})_2Sn(MA)^1_2$	—	14,939	11,981	112·4	111·9	79·7				
$(C_6H_5)_2Sn(MA)^1_2$	—					73·0				

[1] Obtained initially. [2] According to data in the literature, M. p. 140–144° [6]. [3] According to data in the literature, m. p. 122° [3]. [4] According to data in the literature, m. p. 20–22°[3] [5] According to data in the literature, m. p. 91–92° [3]. * n_D^{24}; d^{24}.

TABLE 3. PHYSICO-CHEMICAL PROPERTIES OF ORGANO-TIN POLYMERS AND COPOLYMERS

Monomeric compound	m.p. °C	Softening temperature, °C	
		polymer	copolymer
$(CH_3)_2SnOCOC(CH_3)=CH_2$	110	350	195
$(C_2H_5)_2SnOCOC(CH_3)=CH_2$	75·5	185	120
$(n\text{-}C_3H_7)_2SnOCOC(CH_3)=CH_2$	48·5	110	100
$(C_6H_5)_2SnOCOC(CH_3)=CH_2$	68	170–220	
$(CH_3)_2Sn[OCOC(CH_3)=CH_2]_2$	141	does not melt below 350	
$(C_2H_5)_2Sn[OCOC(CH_3)=CH_2]_2$	137	ditto	160–170
$(n\text{-}C_3H_7)_2Sn[OCOC(CH_3)=CH_2]_2$	16	ditto	175
$(n\text{-}C_4H_9)_2Sn[OCOC(CH_3)=CH_2]_2$	50	ditto	235–240

The trialkylstannyl methacrylates $R_3SnOCOC(CH_3)=CH_2$ and the dialkylstannylene dimethacrylates $R_2Sn[OCOC(CH_3)=CH_2]_2$ where $R=C_5H_{11}$, C_6H_{13}, C_7H_{15}, and C_8H_{17} polymerize even at room temperature in the absence of an initiator in the course of a few hours.



б *а*

FIG. 1. Thermomechanical properties (investigated with the help of a consistometer): (a) of copolymers of trialkyl(aryl)stannyl methacrylates with methyl methacrylate (MMA) (1) $(CH_3)_3Sn$ (MA) with MMA (1:1); (2) $(C_2H_5)_3Sn$ (MA) with MMA (1:3); (3) $(C_3H_7)_3Sn$ (MA) with MMA (1:1); (4) ditto (5:95); (5) ditto (10:90); (6) polymer of $(C_6H_5)_3Sn$ (MA); (b) copolymers of dialkyl-(aryl)stannylene dimethacrylates with MMA, (1) $(C_2H_5)_2Sn$ (MA) with MMA(2:98); (2) ditto (5:95); (3) ditto (10:90); (4) ditto (1:1); (5) $(C_4H_9)_2Sn$ (MA) with MMA (1:1).

EXPERIMENTAL PART

Tetramethylstannane. To an ethereal solution of methylmagnesium iodide, prepared from 48·6 g of magnesium and 284 g of methyl iodide, 90 g of tin tetrachloride were added with cooling and stirring in the course of 30 min, after

which the reaction mixture was boiled for 2 hr. The liquid products were distilled off from the reaction mixture, and from these, after repeated fractionation, 42 g of tetramethylstannane were isolated. B.p. 77–78/761 mm; n_D^{20} 1·4400; d_4^{20} 1·2815; *MR* (found) 37·42, *MR* (calc.) 36·92.

Trimethylbromostannane. In a three-necked flask with a reflux condenser were placed 30 g of tetramethylstannane, and 24 g of bromine were introduced with strong cooling (dry ice). Thereupon, 33·5 g of trimethylbromostannane separated out in the form of lilac-coloured acicular crystals (m.p. 27·0°; yield 82 per cent of theoretical).

Trimethylstannol. In a two-necked flask were placed 11 g of 50% aqueous caustic soda and 20 ml of ether. With continuous stirring, 10·5 g of trimethylbromostannane were added from a dropping funnel. A voluminous flocculent white precipitate was formed and was filtered off. After being dried in a vacuum desiccator, the precipitate was transferred in small portions to a long test-tube with a stopper in which a hole had been made and heated in the flame of a bunsen burner. Fluffy white acicular crystals of trimethylstannol sublimed. The sublimation was continued until drops of moisture appeared on the walls of the tube. The unsublimed portion of the precipitate was treated with several portions of water and ether in order to remove sodium bromide and trimethylstannol residues. The substance remaining was dimethylstannone.

Crystals of trimethylstannol were isolated from the ethereal layer of reaction products after evaporation of the ether.

Found %: C 20·44; 20·31; H 5·69, 5·49

$C_3H_{10}SnO$. Calculated %: C 20·44; H 5·59

Trimethylstannol is readily soluble in alcohols, water, ether, dioxan, benzene and acetone and is insoluble in isopentane.

Trimethylstannyl methacrylate. In a conical flask were placed 1·8 g of trimethylstannol and 1–2 ml of water, and 0·9 g of freshly distilled methacrylic acid was added. A white crystalline precipitate separated and this was washed with several portions of water in order to remove methacrylic acid and was dried in a vacuum desiccator to constant weight. There were obtained 1·9 g of trimethylstannyl methacrylate; m. p. 110°, yield 76·6 per cent of theoretical.

The trialkyl(aryl)stannyl methacrylates indicated in Table 2 were prepared in a similar way.

Trimethylbutoxystannane. To 5 g of trimethylstannol were added 9·5 g of absolute *n*-butyl alcohol. After fractionation of the mixture, a fraction was isolated with b. p. 175–176°/760 mm; n_D^{20} 1·4575; d_4^{20} 1·2656; MR_D (calc). 52·0; MR_D (found) 51·55, which was trimethylbutoxystannane; yield 73 per cent of theoretical. Trimethylbutoxystannane is a colourless mobfle liquid, readily hydrolyzed even in the presence of traces of atmospheric moisture; it distills without decomposition at atmospheric pressure.

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Trimethylacetoxystannane. To 4·5 g of trimethylstannol dissolved in 3 ml of water were added 1·8 g of glacial acetic acid. The seperation of 4·9 g of a white precipitate of trimethylacetoxystannane, m.p. 185°, was observed; yield 83 per cent of theoretical. Trimethylacetoxystannane is insoluble in water.

Dimethyldibromostannane. Bromination of tetramethylstannane was carried out in carbon tetrachloride. To 23 g of tetramethylstannane were added 6·55 ml of bromine at room temperature and the mixture was left overnight. On the following day, a further 6·55 ml of bromine, dissolved in the same quantity of carbon tetrachloride, was added. The reaction mixture was heated for one hour on the water bath. After cooling, 20 g of dimethyldibromostannane separated out in the form of crystals with m.p. 74·0° and b.p. 209/760 mm; yield 50·1 per cent of theoretical.

Dimethylstannylene dimethacrylate. To an aqueous solution of 3·5 g of methacrylic acid were added 2·7 g of dimethylstannoxide, obtained by the hydrolysis of trimethylbromostannane, as shown above, in the synthesis of trimethylstannol or by the hydrolysis of dimethyldibromostannane with aqueous alkali [5]. The mixture was heated to 60–70° during 2–3 min, upon which dimethylstannylene dimethacrylate separated in the form of crystals, which were washed with water and dried in the vacuum desiccator. There were obtained 4 g of dimethylstannylene dimethacrylate with m. p. 143°.

Tetra-n-propylstannane. To the organomagnesium compound obtained from 246 g of *n*-propyl bromide, 48·6 g of magnesium and 300 ml of ether were added 65 g of tin tetrachloride diluted with benzene in the ratio 1:1. The reaction mixture was heated for 3 hr and was then decomposed with an aqueous solution of ammonium chloride and 5% hydrochloric acid. After fractionation there were obtained 45 g of tetra-*n*-propylstannane, b.p. 112–113°; n_D^{20} 1·4742; d_4^{20} 1·1086; MR_D (found) 73·72, MR_D (calc.) 73·96; yield 50·3 per cent of theoretical.

The production of tri-*n*-propylbromostannane and other derivatives was carried out by the bromination of trialkyl- and tetra-alkylstannanes with bromine at −30 or −40° and subsequent fractionation.

Hydrolysis of tri-n-propylbromostannane. In a two-necked flask with a reflux condenser were placed 10 g of tri-*n*-propylbromostannane and 20 ml of ether, and then 12 g of a 30% aqueous solution of caustic soda were added from a dropping funnel with continuous stirring. Thereupon, 3 g of di-*n*-propyl stannone separated out in the form of a white flocculent precipitate, which was filtered off and dried to constant weight. After fractionation of the ethereal solution, 5 g of hexapropylstannoxide and 1 g of tetra-*n*-propylstannane were isolated.

Hydrolysis of tri-n-butylbromostannane. In the hydrolysis of 7·4 g of tri-*n*-butylstannane in a similar manner, there were obtained 0·13 g of di-*n*-butyl stannone (yield 10 per cent of theoretical), 0·9 g of hexa-*n*-butylstannoxide (yield 30 per cent of theoretical), b. p. 186·5–187/3 mm; n_D^{20} 1·4860; d_4^{20} 1·1712; MR_D (found) 146·36, MR_D (calc.) 146·4; mol. wt. (cryoscopic, in benzene) 533·9, mol. wt. (cal-

culated) 596·07, and 0·34 g of tetra-*n*-butylstannane, b.p. 225–229/756 mm; n_D^{20} 1·4735; d_4^{20} 1·0559; MR_D (found) 92·3, MR_D (calc.) 92·2.

Polymerization and copolymerization of trialkyl(aryl)stannyl methacrylates and dialkyl(aryl)stannylene dimethacrylates with unsaturated compounds. The polymerization of trimethyl- and triethylstannyl methacrylates was carried out in ampoules in the presence of 0·1-0·2 per cent of benzoyl peroxide and azobutyronitrile during 24 hr in a thermostat with a temperature of from 80 to 160°, the temperature being raised by 10° every 3 hr. Diethylstannylene dimethacrylate was also polymerized in the thermostat, at a temperature of 130 to 160°. Azobutyronitrile in an amount of 0·2 per cent was employed as the initiator. The polymerization of tripropyl- and triphenylstannyl methacrylates and of dipropyl-, dibutyl- and diphenylstannylene dimethacrylates was carried out in a similar way. We also investigated the copolymerization of the organo-tin mono- and dimethacrylates with methyl methacrylate. Solid, transparent, glass-like products were obtained as a result of these polymerizations and copolymerizations. Some of their properties are given in Table 3. On the addition of 5–10 per cent of dialkylstannylene dimethacrylates, for example, diethylstannylene dimethacrylate, to methyl methacrylate and subsequent polymerization a transparent solid product is obtained which possesses a Vicat heat capacity of 118–125°, a Brinel hardness of 24·5 kg/mm² and a specific resilience of 25·9 kg/cm/cm². Polymerization of dry organo-tin alkyl methacrylates (alkyl from C_5H_{11} to C_8H_{17}) takes place at room temperature in the course of a few hours in the absence of initiators, with the formation of transparent semi-solid gels.

The authors express their thanks to M. F. Shostakovskii for kind assistance in carrying out the work.

CONCLUSIONS

(1) The trialkyl(aryl)stannyl methacrylates $R_3SnOCOC(CH_3)=CH_2$ and the dialkyl(aryl)stannylene dimethacrylates $R_2Sn[OCOC(CH_3)=CH_2]_2$, where R = $=CH_3-$, C_2H_5-, C_3H_7-, *n*-C_4H_9-, *iso*-C_4H_9-, *iso*-$C_5H_{11}-$, $C_6H_{13}-$, $C_7H_{15}-$, $C_8H_{17}-$ and C_6H_5- have been synthesized.

(2) The existence has been established of a disproportionation reaction in the hydrolysis of trialkyl(aryl)halogenostannanes with aqueous alkali solutions, which leads to the formation of dialkyl(aryl)stannones R_2SnO, hexa-alkyl(aryl)stannoxides $R_3SnOSnR_3$ and tetra-alkyl(aryl)stannanes R_4Sn.

(3) It has been found that trialkyl(aryl)stannyl methacrylates and dialkyl (aryl)stannylene dimethacrylates polymerize and copolymerize with various monomeric compounds to form transparent solid or rubber-like substances.

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POLYALUMODIMETHYLSILOXANES*

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THE first information on polymetallo-organosiloxanes appeared in 1957 [1]. Later, work was published on the production of polyalumo-organosiloxanes based on di-and trifunctional organosilicon compounds by means of their co-hydrolysis with aluminium chloride or their reaction with metallic aluminium [2], and also by the method of double decomposition of sodium salts of organosilicon compounds with aluminium chloride [3].

In the present work, new polymers are studied—polyalumodimethylsiloxanes, synthesized by means of the double decomposition of sodium salts of the dimethylsiloxane series according to the following reaction scheme:

$$n(CH_3)_2SiO + 2NaOH \longrightarrow NaO[Si(CH_3)_2O]_nNa + H_2O \quad (1)$$

$$3NaO[Si(CH_3)_2O]_nNa + 2AlCl_3 \longrightarrow \left\{ -O-Al(O_{0,5})-[O-Si(CH_3)_2-]_{1,5n} \right\}_x + 6NaCl \quad (2)$$

Polyalumodimethylsiloxanes have been synthesized according to this scheme in which, from the results of chemical analysis, the Si/Al ratio is 0·8 (A), 1·3 (B), 3·2 (C), 6·8 (D) and 23·3 (E).

The synthesis of polymers so different in composition was carried out with the object of tracing the influence of aluminium on some properties and the structure of the polymers. It has been shown earlier [4] that polyalumo-organosiloxanes obtained from trifunctional organosilicon compounds, in particular, ethyl- and phenyltrichlorosilanes, which possess good solubility in organic solvents, do not melt up to 500° and above. This non-correspondence between the solubility and the fusibility of polyalumoethylsiloxanes and polyalumophenylsiloxanes is connected with the cyclic structure of the chain of their molecules.

The polyalumodimethylsiloxanes synthesized by us, obtained in the form of solutions, were stable. However, after removal of the solvent, their solubility is dependent on the chemical composition of the elementary link of the polymer. Thus, polymers A and B, after evaporation of the solvent, form brittle solid substances insoluble in organic solvents. These polymers are therefore extremely labile, since on removal of the solvent, even in vacuum at room temperature, they pass into an insoluble state. Polymer C, after removal of the solvent, retains

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the capacity of dissolving partially in polar solvents but does not dissolve in non-polar solvents. Polyalumodimethylsiloxanes D and E retain their solubility both in polar and in non-polar solvents even after heat-treatment at 150° for 6 hr. Data on the solubility of the polyalumodimethylsiloxanes are presented in Table 1.

TABLE 1. SOLUBILITY OF POLYALUMODIMETHYLSILOXANES

Polymer	Si/Al ratio	Solubility in								
		Acetone	methyl alcohol	ethyl alcohol	butyl alcohol	CCl_4	benzene	toluene	ether	chloro-benzene
A	0·8	–	–	–	–	–	–	–	–	–
B	1·3	–	–	–	–	–	–	–	–	–
C	3·2	+–	+	+–	+–	–	–	–	–	–
D	6·8	+	+	+–	+–	+–	+–	+–	–	–
E	23·3	+	+	+	+	+	+	+	+	+–
Polyalumo-phenylsiloxane	4·1	+	+	+	+	+	+	+	+	+

The sharp distinction between polyalumodimethylsiloxanes with a Si/Al ratio of up to 3 (A and B) and polyalumoethylsiloxanes and polyalumophenylsiloxanes with a Si/Al ratio of 4 attracts attention; the latter are readily soluble even after heating at 150° for 10 hr. This difference in the properties of the two types of polymers is connected with the different structure of their molecules: polyalumosiloxanes A, B and C, in spite of the fact that they are obtained from the difunctional monomer dimethyldichlorosilane, develop a complex structure more readily than the polyalumoethylsiloxanes obtained from the trifunctional monomer ethyltrichlorosilane.

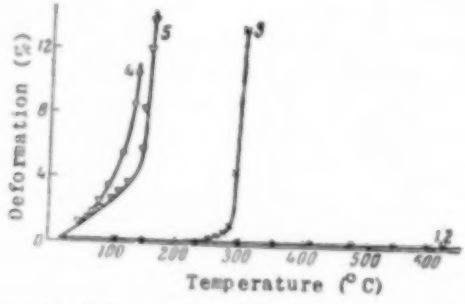

FIG. 1. Thermomechanical properties of polyalumodimethylsiloxanes A, B, C, D, E. (1) A, (2) B, (3) C, (4) D, (5) E.

Investigation of the thermomechanical properties of the polyalumosiloxanes gave the results shown in Fig. 1. It can be seen from Fig. 1 that polymers A and B

do not flow and do not even soften in the range of temperatures from 20 to 250°, that is, they behave as three-dimensional polymers. Plasticizing polymer B with pentachlorodiphenyl does not lead to an increase in the flow of the polymer. The thermomechanical properties for the polyalumosiloxanes C, D and E point to the absence of three-dimensional polymers, which agrees with the solubility data.

Investigation of the polyalumodimethylsiloxanes showed that a definite regularity is observed in the infra-red absorption spectra of polymers A, B, C, D and E, connected with the content of aluminium in them. The absorption bands in the range 980–1100 cm^{-1}, corresponding to the vibrations of the Si—O—Si and Si—O—Al bonds are shown in Fig. 2. It can be seen from Fig. 2 that, with an increase in the ratio of the content of silicon to aluminium in the polymer from 0·8 to 23·3, a shift of the absorption bands in the direction of lower frequencies is observed; the remainder of the spectrum within the limits 700–4000 cm^{-1} does not change.

An intense absorption with a maximum —1070 cm^{-1} is observed for polymer E. An increase in the aluminium content leads to a gradual shift of the absorption maximum to 1000 cm^{-1} for polymer A, in which the Si/Al ratio ~ 1. However, for all polymers studied, the absorption lies within limits not above 1070 cm^{-1}. In Fig. 3, the spectra of polymers E and C are compared with the spectrum of a

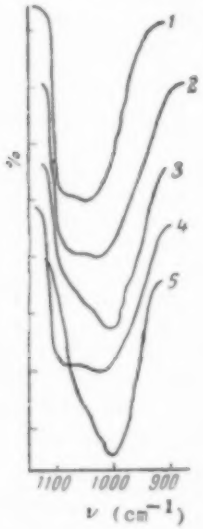

FIG. 2. Change in the infra-red spectra of polyalumodimethylsiloxanes A, B, C, D, E as a function of their composition. (1) A, (2) B, (3) C, (4) D, (5) E.

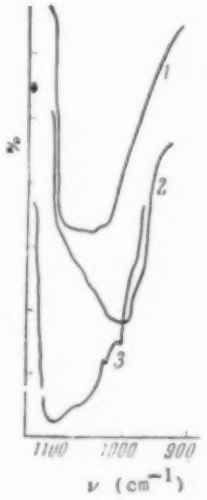

FIG. 3. Infra-red spectra of polyalumodimethylsiloxanes C and E. (1) E, (2) C, (3) polyalumophenylsiloxane (Si/Al ratio = 4)

polyalumophenylsiloxane obtained from the trifunctional monomer phenyltrichlorosilane. The absorption band for the polyalumophenylsiloxane is strongly

shifted in the direction of higher frequencies to 1110 cm^{-1}. This sharp displacement in the absorption bands of the infra-red spectrum of polyalumophenylsiloxane is connected, apparently, with the cyclo-linear structure of the polymer molecules, which consist predominantly of polyalumodimethylsiloxane rings. The displacement of the absorption bands for polyalumodimethylsiloxanes with Si/Al ratios of 0·8 and 3·2, that is, less than and close to the ratio for polyalumophenylsiloxane, is connected with the different structure of the molecules of these polymers. On the basis of the thermomechanical properties, the solubility data and infra-red spectroscopy, it may be assumed that the polyalumodimethylsiloxanes are, structurally, branched molecules which contain fewer polyalumoorganosiloxane rings than the polyalumophenylsiloxanes and the polyalumoethylsiloxanes.

EXPERIMENTAL PART

Hydrolysis of dimethyldichlorosilane. Water was placed in a glass hydrolyser provided with an external jacket for cooling the water, a mechanical stirrer, a dropping funnel and a thermometer, and the dimethyldichlorosilane was introduced from the dropping funnel with continuous stirring. In this work, dimethyldichlorosilane with a chlorine content of 55·4–55·6 per cent was used (theoretical chlorine content 54·98 per cent). The water taken for the hydrolysis was twice the amount of the dimethyldichlorosilane. The rate of introduction of the dimethyldichlorosilane and the intensity of the cooling of the reaction mixture were adjusted in such a way that the temperature of the hydrolysis did not exceed 25°. After the introduction of the dimethyldichlorosilane was complete, the mixture was stirred for 1 hr. The polydimethylsiloxane obtained was separated from the aqueous layer and washed repeatedly with water until the wash waters showed a neutral reaction to Congo red, after which it was dried with calcium chloride and filtered.

Preparation of sodium salts of the polydimethylsiloxane series. The product of the hydrolysis of dimethyldichlorosilane was placed in a beaker and NaOH in the form of a 49–51% aqueous solution was added. The calculation of the reactants was carrried out according to equation (1), given above. The mixture was stirred vigorously (during which it became thicker), after which it was dried in vacuum initially at 50–60° and finally at 70–80°. Salts of the probable general formula $Na[Si(CH_3)_2O]_nNa$, possessing the characteristics shown in Table 2, were obtained.

Preparation of polyalumodimethylsiloxanes. In a three-necked flask, provided with a reflux condenser, dropping funnel and thermometer, was placed a 15–20% solution of the sodium salt of polydimethylsiloxane in a mixture of ethyl alcohol and toluene (1:1). The solution was heated with stirring to 60–65°, after which the heating was discontinued and a 10–15 per cent solution of aluminium chloride in absolute ethyl alcohol was added in small portions from the dropping funnel.

TABLE 2. COMPOSITION OF THE SALTS OBTAINED

No. in series	n	Na content (%)	
		found	calculated
1	1	38·9	33·8
2	1	34·0	33·8
3	2	19·3	21·9
4	4	13·8	12·8
5	4	11·6	12·8

The aluminium chloride taken for the reaction was 75–80 per cent of the amount calculated from equation (2) in order to ensure the alkaline character of the reaction medium. The mixture was stirred until the temperature had fallen to that of the room, the separation of a precipitate of sodium chloride, in an amount close to that calculated, being observed; the precipitate was filtered off. the yield of polymers amounted on the average to 50–70 per cent. The following polyalumodimethylsiloxanes were isolated (with drying at room temperature in vacuum).

Polyalumodimethylsiloxane A. Obtained from sodium salt No. 1. Chemical composition(%): Si 14·59, 14·78; Al 18·59, 18·32; C 14·95, 14·91: H 5·69, 5·49. The polymer is insoluble in polar and non-polar solvents.

Polyalumodimethylsiloxane B. Obtained from sodium salt No. 2. Chemical composition (%): Si 22·32, 22·22; Al 16·80; C 18·23, 18·08; H 4·54, 4·78. The polymer is insoluble in polar and non-polar solvents.

Polyalumodimethylsiloxane C. Obtained from sodium salt No. 3. Chemical composition (%): Si 25·68, 25·53, Al 7·75, 7·61; C 24·05, 24·06; H 6·89, 7·27; The polymer partially dissolves in acetone and ethyl, butyl and methyl alcohols; it does not dissolve in non-polar solvents.

Polyalumodimethylsiloxane D. Obtained from sodium salt No. 4. Chemical composition (%): Si 30·18, 29·70; Al 4·36, 4·12; C 25·91, 25·55; H 7·49, 7·41. The polymer dissolves in acetone and methyl alcohol, and dissolves partially in ethyl and butyl alcohols, carbon tetrachloride, benzene and toluene.

Polyalumodimethylsiloxane E. Obtained from sodium salt No. 5. Chemical composition (%): Si 26·18, 26·37; Al 1·09, 1·09; C 24·85, 24·84; H 6·99, 7·20. The polymer dissolves in acetone, methyl, ethyl and butyl alcohols, carbon tetrachloride, benzene, toluene and ether, and dissolves partially in chlorobenzene.

*Investigation of the thermomechanical properties of the polyalumodimethylsiloxanes** was carried out by the method described [5] with a specific loading — 1 kg/cm². The rate of temperature increase was 70° per hr.

* The thermomechanical curves were determined by G. Ye. Golubkov and the infrared spectra by N. P. Gashnikova, to whom the authors render their profound thanks.

Infra-red absorption spectra were taken on a UR-10 spectrometer with NaCl and KBr prisms. The soluble products were examined in the form of 1·5 per cent solutions in CCl_4 and the insoluble ones in the form of a paste with vaseline oil. In the latter case, the thickness of the absorbing layer was not regulated.

CONCLUSIONS

(1) New polymers—polyalumodimethylsiloxanes—were synthesised and their properties studied. It was found that the growth of a more complex structure in the polyalumodimethylsiloxanes on heating takes place more readily the greater the content of aluminium in the polymer molecule.

(2) The solubility, thermomechanical properties and infra-red absorption spectra of the polyalumodimethylsiloxanes were studied. A hypothesis on the structure of the polymer molecules has been made.

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AN INVESTIGATION OF FREE RADICAL REACTIONS IN IRRADIATED POLYTETRAFLUOROETHYLENE—I. THE APPLICATION OF THE ELECTRONIC PARAMAGNETIC RESONANCE METHOD IN INVESTIGATING RADICAL CONVERSIONS AND THE DETERMINATION OF THE DIFFUSION COEFFICIENT FOR OXYGEN IN POLYTETRAFLUOROETHYLENE*

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IN the course of recent years the electronic paramagnetic resonance (EPR) method has been applied with success in elucidating the structure of free radicals formed when initiating radiation acts on solids. During this work it was discovered that the stability of free radicals and consequently their maximum concentration depends very strongly both on the actual properties of the radicals formed and on the properties of the solid *matrix* surrounding them. The most important parameter characterizing the properties of the matrix in relation to radical recombination is the coefficient of diffusion of the individual molecules in the matrix.

However, to study the chemical activity of the radicals in the matrix in question it was necessary to find a method of measuring the velocity constants of the individual elementary reactions of these radicals after having at the same time excluded the influence of diffusion. The solution of these general problems was undertaken by us on the basis of an investigation of the properties of the radical system formed on irradiating polytetrafluoroethylene (teflon). It was shown previously [1,2] that under the influence of irradiation very stable radicals, capable of transformation into very stable peroxide radicals on interaction with oxygen, are formed in this substance. The feasibility of exact measurement of the changes in the concentrations of both radicals by the EPR method in the course of the process leads us to the idea that this was just the example in which separation of diffusion and the process of interaction of the radical with the molecules of the gas phase could be performed. In the present communication some features of kinetic measurements made by us by the EPR

* Vysokomol.soedin. **1**: No. 10, 1519–1525, 1959.

method are described and results on the determination of the coefficient of diffusion of oxygen in teflon are given. Since such data do not, as far as we know, exist in the literature, they may be of interest in themselves. On the other hand, the determination of exact values for the diffusion coefficient of oxygen in teflon has enabled us, as will be shown in the following communication, to determine the value of the velocity constant of the elementary radical reactions in irradiated teflon.

INTRODUCTION

As was shown earlier [1, 2], the action of ionizing radiation on teflon leads to the breaking of C–F bonds and the formation of radicals of the $CF_2-\dot{C}F-CF_2$ (R) type, the EPR spectrum of which is a partial superposition of two *quintuplets* with a ratio of the intensities of the components of 1 : 4 : 6 : 4 : 1 at temperatures above 0°C. The interaction of the radicals R with oxygen leads to the formation of peroxide radicals of the RO_2 type, the spectrum of which is an assymetric singlet with $g_{cp}=2{\cdot}017\pm0{\cdot}003$. Both the radicals $\dot{R}$ and $\dot{R}O_2$ are very stable right up to temperatures near the melting point of teflon ($\sim$320°C). The EPR spectra can easily be identified in their case even in the case of superposition, which permits one, as will be shown below, to perform quite accurate measurements in a wide range of temperatures and of $\dot{R}$ and $\dot{R}O_2$ concentrations. All this considerably widens the possibilities of investigating their conversions.

EXPERIMENTAL TECHNIQUE

The experiments were carried out on an EPR spectrometer with high frequency modulation of the magnetic field operating at a wavelength of 3·2 cm with a cylindrical resonator of the H_{011} type [3]. The specimen was placed on the bottom of a special glass ampoule connected with a vacuum system for evacuation and admission of gases (Fig. 1). The temperature of the specimen was maintained by blowing a jet of heated air or nitrogen around the ampoule containing the specimen. Inspection of the temperature was achieved by a thermocouple mounted in a thin quartz capillary so that the weld was at the centre of the specimen. All the measurements of the intensities of the EPR lines were performed with reference to a standard for which a single crystal of the salt $CuCl_2{\cdot}2H_2O$ was used. The single crystal was orientated in the magnetic field in a manner such that the paramagnetic absorption line of the standard did not superimpose on the spectrum of the radicals $\dot{R}$ and $\dot{R}O_2$. The $CuCl_2{\cdot}H_2O$ monocrystal was sealed into a flat capillary which was in turn fixed in a round capillary. On performing measurements at various temperatures the temperature of the standard was kept the same by blowing a jet of cold air round the round capillary.

In our measurements specimens of teflon irradiated in vacuum at 77°K on a γ-source of ^{60}Co with a dose of ~20 Mr were used. Some of the experiments were carried out on specimens irradiated with a dose of 40 Mr, but no important differences were discovered in the results obtained on increasing the dose. To

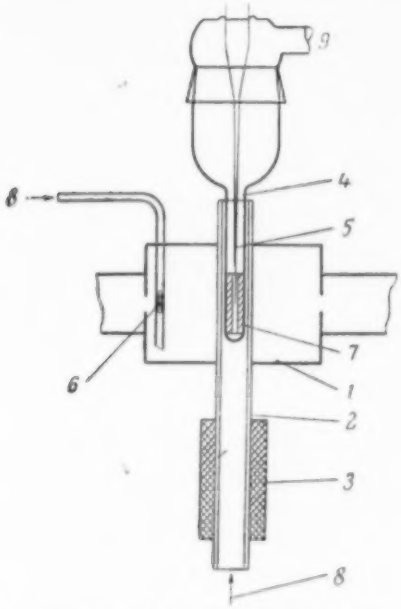

FIG. 1. System for evacuating, admitting gases and thermostating specimens in the resonator. (1) Resonator; (2) Quartz tube; (3) Furnace; (4) Glass ampoule; (5) Copper-constantan thermocouple; (6) ($CuCl_2 \cdot 2H_2O$) standard; (7) Sample; (8) To air compressor; (9) To vacuum system.

study diffusion specimens in the form of a cylinder with $d = 3{\cdot}5$ mm and $l = 15$ mm were used. In the course of the experiments we also made use of the circumstances that at temperatures of 150–200°C the equilibrium $\dot{R} + O_2 \rightleftharpoons \dot{R}O_2$ is displaced towards the $\dot{R}$ side to a significant degree, which permits one to convert RO_2 completely to R at these temperatures in the course of a few hours and thus to re-establish the original properties of the specimen. To obtain more complete data we performed measurements on a series of teflon specimens irradiated in identical conditions. The results obtained on different specimens agree quite satisfactorily.

THE TECHNIQUE OF QUANTITATIVE CALCULATION FROM THE EXPERIMENTAL DATA

A typical record of the first derivative of the spectrum of one of the investigated specimens containing R and RO_2 is shown in Fig. 2. In all the measurements it was assumed that the amplitude of the first derivatives of the lines

I_α and I_β are proportional to the concentrations of the radicals RO_2 and R respectively. More accurate relationships may be written in the form:

$$[\dot{R}O_2] = \gamma_\alpha \omega_\alpha^2 I_\alpha$$
$$[\dot{R}] = \gamma_\beta \omega_\beta^2 I_\beta, \qquad (1)$$

where I_α, and I_β are the amplitudes of the first derivatives of the corresponding lines; ω_α and ω_β are the widths of the respective lines; γ_α and γ_β are coefficients

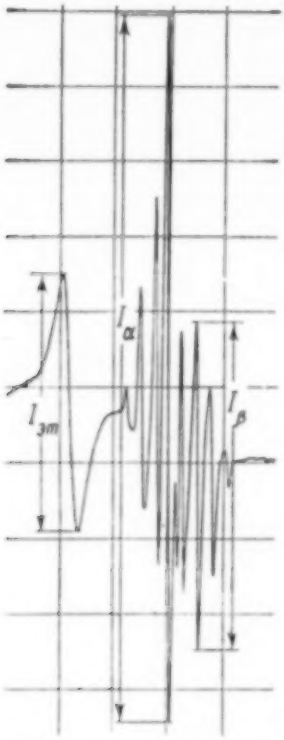

FIG. 2. The spectra of radicals R and RO_2. The standard signal is on the left.

depending on the form of the lines, the number of components and their relative intensities in the EPR spectra of the $\dot{R}O_2$ and $\dot{R}$ radicals.

In all the measurements we suppose that the coefficients γ_α, γ_β, ω_α, ω_β do not vary with time in the course of diffusion or reaction. If the change in one or both of the concentrations with time is fixed in an experiment, as for example in the case of diffusion, then the law of conservation for the radicals gives

$$[\dot{R}] + [\dot{R}O_2] = [\dot{R}]_0$$

where $[\dot{R}]_0$ is the initial concentration of $\dot{R}$. Substituting (1) we find:

$$I_\alpha + \frac{\gamma_\beta \omega_\beta^2}{\gamma_\alpha \omega_\alpha^2} I_\beta = (I_\beta)_\alpha \frac{\gamma_\beta \omega_\beta^2}{\gamma_\alpha \omega_\alpha^2}.$$

Putting $\frac{\gamma_\beta \omega^2}{\gamma_\alpha \omega_\alpha^2} = \beta$, we obtain:

$$I_\alpha + \beta I_\beta = \beta (I_\beta)_0. \tag{2}$$

In the case of kinetic investigations (3) it is often very important to know, not the values of R and RO_2 themselves, but their ratio R/RO_2. From (1) it follows directly that

$$\frac{[\dot{R}]}{[RO_2]} = \beta \frac{I_\beta}{I_\alpha} \tag{3}$$

The coefficient takes account of the difference in the widths and shapes of the lines and in the number of components in the EPR spectra of the radicals R and RO_2. Supposing $[\dot{R}] = \beta I_\beta$ and $[RO_2] = I_\alpha$ respectively, we shall express the concentrations in relative, but identical units. The dependence on temperature obviously also enters into (2) and (3) by way of β since the quantities entering into the expression for β may depend on temperature.* The linear

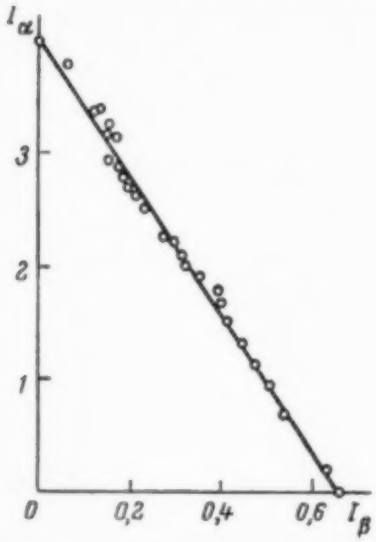

FIG. 3. Verification of relationship (2) for the process of diffusion (diffusion in a cylinder at 43°C).

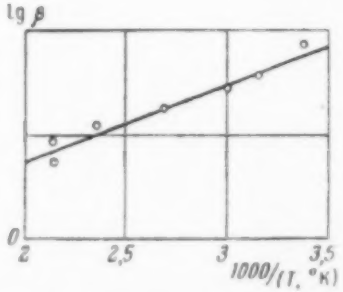

FIG. 4. The temperature variation of the coefficient β; $\varepsilon_\beta = 1{\cdot}5 \pm 0{\cdot}5$ kcal/mole.

* In this examination we shall suppose that the variations of I_α and I_β with temperature according to the Curie-Weis law coincide, which is valid, generally speaking, if one supposes $\Theta_{\dot{R}} \neq \Theta_{RO_2}$. Since for radicals of the type investigated $\Theta \approx 0$ this the approximation is apparently justified. If, however, $\Theta_{\dot{R}} \neq \Theta_{RO_2}$, all the considerations remain the same with the exception that an additional dimensionless multiplier depending on temperature $(T - \Theta_{RO_2})/(T - \Theta_{\dot{R}})$ enters into β. Since, as will be shown below at various temperatures β is determined directly from the experimental data, the possible influence of this multiplier is automatically taken account of in our examination.

relation between I_x and I_β (2) was checked experimentally in the course of different processes leading to a change in the concentrations of R and RO_2 in the specimen (diffusion of oxygen, establishment of the equilibrium $[\dot{R}]+[O_2]$ $[\dot{R}O_2]$, removal of oxygen). In all cases the relationship (2) is obeyed with accuracy within the experimental error. One of the experimental variations for the case of oxygen diffusion is reproduced in Fig. 3. By the same method the values of β at various temperatures were found. From the graph of $\log \beta$ against $1/T$ (Fig. 4) it follows that the dependence of β on temperature is satisfactorily described by an exponential law. From the experimental data it was found that

$$\beta = 0{\cdot}4e^{1500 \pm 500/RT}.$$

Making use of this expression and equation (2) we therefore have the possibility of expressing the concentrations $\dot{R}$ and $\dot{R}O_2$ at different temperatures in the same relative units, starting from the corresponding values of I_x and I_β.

DETERMINATION OF THE DIFFUSION COEFFICIENT FOR OXYGEN IN IRRADIATED TEFLON

The diffusion of oxygen in irradiated teflon is accompanied by the reaction $\dot{R}+O_2 \rightarrow \dot{R}O_2$. If the diffusion time at the same time considerably exceeds the reaction time, then the rate of formation of RO_2 radicals, equal to the rate of disappearance of R, will be determined not by the velocity constant of this reaction, but by the diffusion velocity of oxygen into the specimen. As is shown below, for a cylindrical specimen of diameter 3·5 mm the diffusion time at room temperature and at atmospheric pressure amounts to ~ 200 min, while the reaction time in the same conditions is ~ 10 sec. From this it follows that in the case of sufficiently massive specimens one can follow the diffusion of oxygen in the specimen directly by the course of the kinetics of transformation of R into RO_2. At the same time in view of the high velocity of the $\dot{R}+O_2 \rightarrow \dot{R}O_2$ process one can consider, as will be shown below, that in the part of the specimen into which a sufficiently large quantity of oxygen has managed to diffuse at the moment of time t practically all the radicals R have changed into RO_2.

An investigation of the diffusion of oxygen into irradiated teflon was performed in the temperature range 23°–200°C at atmospheric pressure. In Fig. 5 the kinetic diffusion curves are reproduced in I_x, βI_β & t coordinates. As is evident from Fig. 6, in quite a wide conversion range a linear dependence of the radical concentrations on $\sqrt{t}$ prevails. In the whole range of temperatures investigated reciprocity of the increase in concentration of RO_2 with fall in R is observed.

In addition, as was pointed out earlier, complete regeneration of R by pumping out the specimen at 150–200° occurs. These two results indicate the absence of any additional processes leading to the destruction of R or RO_2 in these conditions.

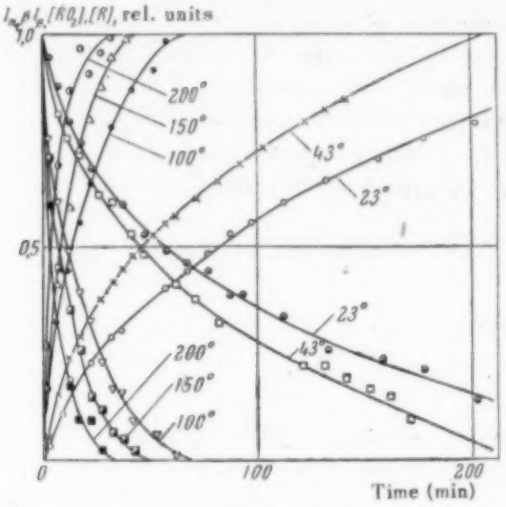

FIG. 5. The kinetics of oxygen diffusion in irradiated teflon at various temperatures.

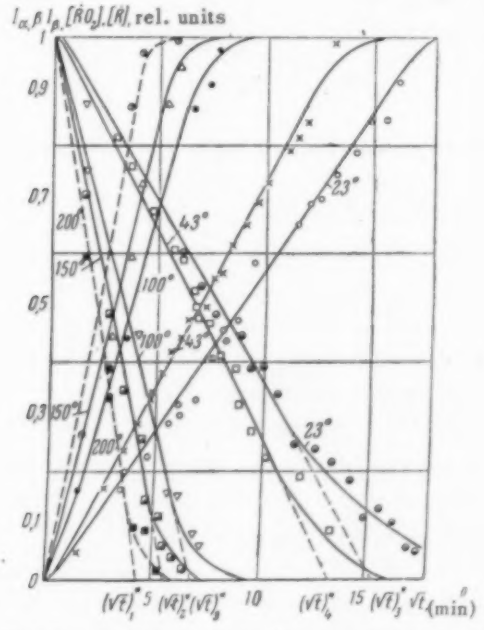

FIG. 6. Families of curves of the kinetics of oxygen diffusion.

To explain the experimentally observed kinetic curves for the change in RO_2 and R and to calculate the diffusion coefficient for oxygen from them let us examine how the average concentration of the RO_2 radical determined when

the depth of penetration of oxygen into the specimen fulfils the conditions indicated above is connected with the distance to which an oxygen molecule has diffused in the time t. Let a molecule of oxygen diffuse into an ordinary unirradiated specimen of teflon in time t to a distance $x=r_0-r$, where r_0 is the radius of the cylinder.* The average concentration of $\dot{R}O_2$ throughout the whole specimen may then be written in the form:

$$[\overline{\dot{R}O_2}]_t=[\dot{\overline{R}}]_0\frac{V_x}{V_0}=[\dot{\overline{R}}]_0\frac{r_0^2-r^2}{r_0^2},$$

or for $x \ll r_0$ we have:

$$[\overline{\dot{R}O_2}]_t=2[\dot{R}]_0\frac{x}{r_0}. \tag{4}$$

To find the kinetic law $[\dot{R}O_2]=f(t)$ we make use of the Einstein relationship connecting the average distance to which a particle diffuses in time t with the diffusion coefficient D:

$$x^2=A\cdot Dt, \tag{5}$$

where A is a numerical coefficient depending on the shape of the specimen. From (5) and (4) we find:

$$[\overline{\dot{R}O_2}]_t=2[\dot{\overline{R}}]_0\frac{1}{r_0}\sqrt{ADt} \tag{6}$$

or, changing to the experimentally measured quantities, we obtain:

$$(I_x)_t=2\beta(I_\beta)_0\frac{1}{r_0}\sqrt{ADt}, \tag{7}$$

$$(I_\beta)_t=(I_\beta)_0\left[1-\frac{2}{r_0}\sqrt{ADt}\right]. \tag{8}$$

In I_x, $\beta I_\beta \propto \sqrt{t}$ coordinates the kinetics of diffusion in the initial region must thus actually be linear. It is evident that for large depths of conversions formula (4) will no longer be obeyed since in this case one cannot consider $x \ll r_0$. For $x \simeq r_0$ the problem of the kinetic law $[\dot{R}O_2]=f(t)$ or $[\dot{R}]=\psi(t)$ has no meaning since in this case the ratio $[\dot{R}O_2]/[\dot{R}]$ becomes constant for any given temperature by virtue of the equilibrium $\dot{R}O_2 \rightleftharpoons \dot{R}+O_2$.

Deviation from linearity (Fig. 6) are observed experimentally at $x \simeq 0{\cdot}5\, r_0$. From the kinetic diffusion curves one may calculate the diffusion coefficient for oxygen in irradiated teflon. The slope of the linear sections of the kinetic

* In the case of diffusion through a preliminarily irradiated specimen the diffusion picture remains the same. However, in a layer of thickness x all the R radicals change into RO_2, which is also established by the method used by us. One must bear in mind that in the layer x the concentration of dissolved oxygen is much greater than R and RO_2.

curves (Fig. 6), as follows from formulae (7) and (8), is related to the diffusion coefficient by the following relation:

$$k = 2\beta(I_\beta)_0 \frac{1}{r_0}\sqrt{AD}. \tag{9}$$

If the value of $\sqrt{t}$ corresponding to the intersection of the straight line with the abscissa axis obtained by extrapolation of the linear portion of the $[\dot{R}] = F(\sqrt{t})$ (see Fig. 6) kinetics by $(\sqrt{t})^*$, then for k we have the expression:

$$k = \frac{\beta(I_\beta)_0}{(\sqrt{t})^*}. \tag{10}$$

From (9) and (10) we obtain:

$$D = \frac{1}{4A}\left[\frac{r_0}{(\sqrt{t})^*}\right]^2 \tag{11}$$

For a cylindrical specimen one can assume the coefficient A equal to 5·8 (this value can be obtained by putting the index of the exponent of the first term in the exact solution of the problem of diffusion in a cylinder [4] equal to unity). Having determined the diffusion coefficient at various temperatures from the kinetic data, one can calculate the pre-exponential term and the energy of activation for diffusion. The data are disposed well in a straight line in log D and $1/T$ coordinates (Fig. 7). From the tangent of the slope of the logarithmic

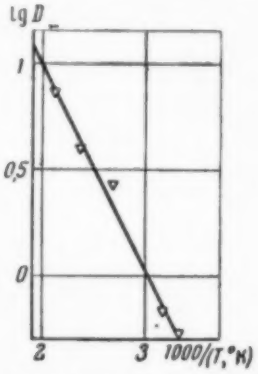

FIG. 7. The temperature dependence of the diffusion coefficient of oxygen in irradiated teflon; ε_d 4·6±0·5 kcal/mole. Co-ordinate axis: 7+log D.

families of curves the energy of activation for diffusion ε_d is determined. The final expression for the diffusion coefficient of oxygen in teflon irradiated with a megaröntgen dose is obtained in the form:

$$D = (1{\cdot}8 \pm 0{\cdot}2)\,10^{-4}\, e^{-\frac{4606 \pm 500}{RT}}\ \text{cm}^2/\text{sec}$$

For a 40 Mr dose measurements were only performed at 163°. The value of D at the same time practically coincides with the value obtained at the same

temperature on a specimen irradiated with a 20 Mr dose. This indicates apparently that the change in dose by times in the given case does not lead to an important change in the lattice.

CONCLUSIONS

The EPR method has been applied in the investigation of the interaction of radicals in the solid phase with molecules of the gas phase. A technique for calculating the kinetic and diffusion constants from the EPR spectrum is proposed.

The diffusion process for oxygen in irradiated teflon has been studied experimentally and the value of the pre-exponential multiplier (D_0) and the energy of activation for diffusion (ε_d) has been found.

Translated by N. G. Anderson

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THE THERMAL DEGRADATION OF POLYPROPYLENE*

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INTRODUCTION

IN connexion with the growth in the production of polypropylene and the diversity of its fields of application, the investigation of its degradation and in particular its thermal degradation is acquiring ever greater importance.

Only one work (and that only partly) [1] has been devoted to the thermal degradation of polypropylene. In that paper the following products of the thermal degradation of polypropylene were revealed by the mass-spectrometer method: C_2H_4, C_3H_6, C_4H_{10}, C_4H_8, pentene, etc. The effective activation energy for the process proved to be 61 kcal/mole.

The present work was performed with the aim of obtaining more detailed information about the mechanism of the thermal degradation of polypropylene. The work consisted in heating the specimens of polypropylene in vacuum. The influence of temperature and addition of inhibitor on the rate of evolution of gaseous products was studied.

TECHNIQUE

The polypropylene, obtained on Ziegler-Natta catalyst, had a molecular weight of 175,000 and a content of isotactic faction of 81 per cent. The product was freed of solvent and adsorbed gases by pumping (10^{-2} mm Hg) for 9 hr at a temperature of 250°C.

The 2,2-Di-*p*-oxyphenylpropane (commercial name—diphenylpropane), a commercial product, purified by recrystallization from acetic acid, had a yellow colour and a melting point of 153°C.

The apparatus in which the experiments were conducted is shown in Fig. 1. The volume of its vacuum section was equal to 370 cm³. The reaction vessel, made of quartz and molybdenum glass, was attached to the apparatus by means of a ground glass joint. The furnace had a uniform temperature region of 16 cm in length. A platinum spiral placed near the heater windings served as a resistance thermometer for an electronic temperature controller which kept the temperature in the furnace constant to an accuracy of ±1°C. By moving the furnace along

* Vysokomol. soedin. **1**: No. 10, 1552–1557, 1959.

the rails it could easily be moved over the reaction vessel and moved away from it. The temperature in the furnace was measured by means of a carefully calibrated thermocouple and potentiometer. The experiments were performed in this apparatus in the following manner: a quartz boat with a weighed amount of purified polymer was placed in the cold part of the reaction vessel and the

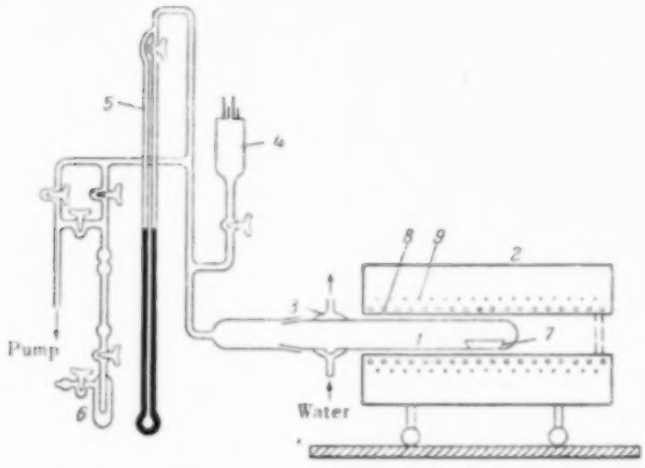


FIG. 1. The apparatus for studying the thermal degradation of polypropylene. (1) Reaction vessel; (2) Furnace; (3) Water cooler; (4) Manometric lamp LT-2; (5) Mercury manometer; (6) Trap; (7) Quartz boat containing polymer; (8) Furnace heater windings; (9) Platinum temperature probe.

apparatus was pumped out to 10^{-2} mm. At the same time the major part of the reaction vessel was heated in the furnace. With the aid of a magnet and iron sealed into the glass the boat was then introduced into the uniform temperature zone. The polymer melted and its degradation began. From this moment on, the pressure and the temperature was measured at specified intervals of time. On finishing an experiment the gaseous products of the degradation were frozen out in a trap cooled with liquid nitrogen, the solid deposit in the boat was weighed; the liquid products condensed in the cold part of the reaction vessel were not analyzed.

The experiments of the degradation of polypropylene with an admixture of 2,2-di-*p*-oxyphenylpropane were performed in the same way. The inhibitor was introduced into the polymer by carefully grinding the two components in a mortar or by dissolving them together in decalene at a temperature of 130–140°C and subsequently distilling off the solvent in vacuum. The method of introducing the inhibitor was not reflected in the kinetics of degradation of the polypropylene.

The composition of the gaseous products of degradation were determined chromatothermographically (2) by means of a thermodynamic chromathermograph calibrated from a gas mixture of known composition. One of the chromatograms obtained in the analysis of the degradation products is reproduced in Fig. 2.

FIG. 2. Chromatogram of the products of the pyrolysis of polypropylene at 400°C. (1) C_3H_6; (2) C_4H_8; (3) $C_5H_{10} + C_5H_{12}$.

EXPERIMENTAL RESULTS

Our experiments showed that at temperatures below 300°C degradation of polypropylene proceeds very slowly. The rate of gas evolution w_0 for low conversion depths calculated per gram of polymer is practically a constant which depends on temperature. It is expressed as follows:

$$w_0 = \frac{1}{m_0}\frac{dp}{dt} = \text{Const.} \qquad (1)$$

At 412°C polypropylene is almost completely destroyed in 30 min and the weight of the residue amounts to 4 per cent of the weight of the original polymer. The values of w_0 obtained by us for various temperatures are reproduced in Table 1.

TABLE 1. INITIAL RATES OF DEGRADATION OF POLYPROPYLENE

T°C	320	337	350	353	361	362	374	381	383	395	400	403	412
w_0 (mm/g. min)	0·005	0·03	0·08	0·09	0·11	0·17	0·34	0·64	0·63	1·09	1·31	2·36	4·84

As is evident from Table 1, the rate of degradation increases regularly with rise in temperature.

The results on the investigation of the influence of inhibitor additions to polypropylene on the rate w_0 are shown in Table 2.

TABLE 2. THE INITIAL RATES OF DEGRADATION OF POLYPROPYLENE IN THE PRESENCE OF DIPHENYLPROPANE

Quantity of inhibitor (weight %)	0	1	3	5
$w_0 \frac{1}{m_0}\frac{dp}{dt}$ (mm/g.min)	0·090	0·037	0·027	0·010

As follows from Table 2, increase in the concentration of inhibitor leads to a reduction in the rate of destruction.

The results of our analyses of the gaseous products of degradation of polypropylene are reproduced in Table 3. For comparison the results of analyses from [1] are reproduced in the same Table.

TABLE 3. THE MAIN GASEOUS PRODUCTS OF THE DEGRADATION OF POLYPROPYLENE

Content of substance in products of degradation (volume %)	Temperature of experiment (°C)			Results from reference [1]
	400°	380°	350°	
C_3H_6	34	55	52	3–11
C_4H_8	2	6	–	9–23
$C_5H_{10}+C_6H_{12}$	41	39	39	22–43

As is evident from Table 3, the main gaseous products obtained in the thermal degradation of polypropylene are propylene, *iso*butylene and pentene. The remaining products are obtained in smaller quantities.

To elucidate the influence of thermal degradation on the crystallinity of polypropylene we took electronograms of films made from the original polypropylene and from polymer degraded at 360°C. The energy of the electron beam amounted to 60 keV. A print of these electronograms is shown in Fig. 3.

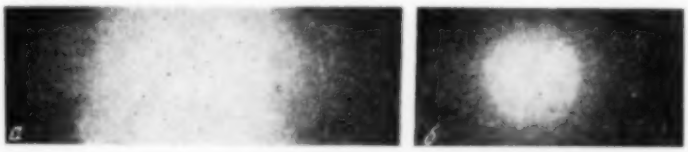


FIG. 3. (a) Electronogram of initial polyprolene; (b) With partial destruction, $T = 360°$.

The sharp diffraction rings on the electronogram of the original polymer (a) reveals its high crystallinity, while the blurring of rings on electronogram (b) provide evidence of considerable amorphization of the polymer as a result of thermal degradation.

DISCUSSION OF RESULTS

Assuming that the initial rate of the reaction in our experiments depends on temperature according to the Arrehnius law:

$$w_0 = Ae^{-E/RT} \qquad (2)$$

we have

$$\log w_0 = \log A - E/4{\cdot}6\,T \tag{3}$$

Here E is the effective energy of activation of the gross thermal degradation process of polypropylene.

The results of our experiments are reproduced in Fig. 4 in log w_0 and $1/T$ coordinates. The experimental points lie on a straight line from the slope of which we determined the value $E = 55$ kcal/mole. This value is near to the value of E found in [1].

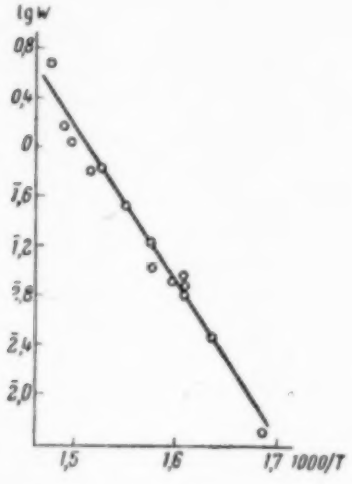


FIG. 4. The dependence of the rate of degradation of polypropylene on temperature in log w_0 and $1/T$ co-ordinates.

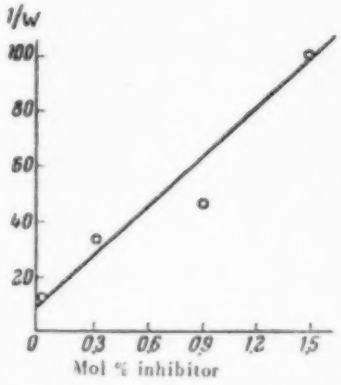


FIG. 5. The dependence of the rate of degradation of polypropylene on inhibitor addition in $1/w_0$ and $[x]$ co-ordinates; $T = 253°C$.

The low value of the activation energy compared with the energy of 80 kcal/mole necessary to break the C—C bond in polypropylene provides evidence of a chain mechanism for the thermal degradation of polypropylene. The same thing is suggested by the nature of the slowing down of the process by additions of 2,2-di-*p*-oxyphenylpropane. Indeed, from the chain theory of inhibition the formula

$$1/w_0 = \frac{w_{\text{init.}}}{\beta + K[x]} \tag{4}$$

follows, where $w_{\text{init.}}$ is the rate of nucleation of active centres, β is the probability of the chain breaking off in the absence of an inhibitor, $[x]$ is the concentration of inhibitor and K is a constant. In the initial period of the reaction the quantities $w_{\text{init.}}$ and $[x]$ may be considered constant. For this condition formula (4) may be written in the form

$$1/w_0 = A + B[x] \tag{5}$$

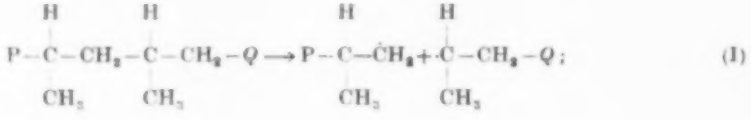
where A and B are constant coefficients for $T = \text{const}$.

In Fig. 5 the results of our experiments cited in Table 2 are represented in $1/w_0$ and $[x]$ co-ordinates. It is evident that the dependence of $1/w_0$ on $[x]$ may be considered linear. This provides evidence for the applicability of formula (4) as must be the case in the case of a chain reaction.

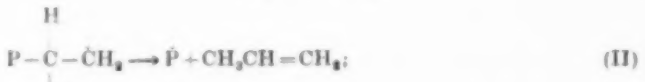
Let us now examine the question of the formation of the gaseous products of the thermal degradation of polypropylene. In agreement with the authors of a number of papers on the theory of polymer degradation [3,4,5] let us assume that the thermal degradation of polypropylene is a chain process which consists of the following elementary reactions: (a) initiation—the breaking of a C—C bond at a random point; (b) continuation of the chain—the breaking off of monomer molecules one after another from the radicals formed in initiation; (c) intermolecular chain transfer—the breaking off of an atom of hydrogen (by a radical) from a neighbouring molecule and the disintegration of the latter; (d) the isomerization of a radical and its subsequent disintegration; (e) breaking off of the chain as a result of disproportionation of two radicals.

Reaction (c) leads to the breaking up of the polymer molecules into parts of comparatively large molecular weight, i.e. to solid prioducts.

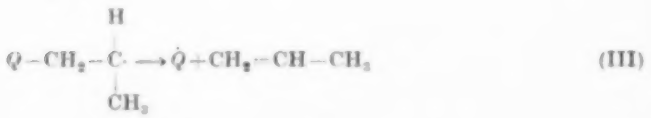
Propylene is formed by reaction (b) according to the following scheme



(I)



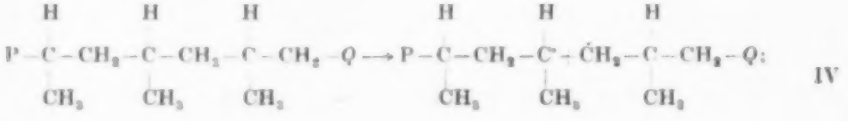
(II)



(III)

Reactions (II) and (III) proceed apparently with an activation energy of ~ 19 kcal/mole, as is, for example, the case in the case of the disintegration of the normal propyl radical into ethylene and a methylene radical [6].

Since large quantities of *iso*butylene and pentene are formed together with propylene in the case of thermal degradation, we think that under our conditions isomerization of radicals according to reaction (d) plays a big role. Apparently neighbouring atoms of hydrogen migrate to the positoin of a free radical with extreme ease according to the scheme:



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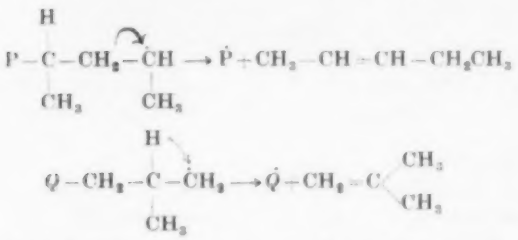

V

VI

As a result *iso*butylene and pentene are formed. Competition of the isomerization reactions (V)d(VI) with the disintegration reactions (II) and (III) may occur since the activation energy for the isomerization process is apparently small and lies around 18 kcal/mole [7]. The presence of considerable quantities of *iso*butylene and pentene in the composition of the gaseous products of the degradation of polypropylene suggests that the isomerization of aliphatic radicals formed in the course of the chain disintegration of polypropylene occurs and plays an important rôle.

In this connection reference [8] should be mentioned. In this it is shown that the thermal degradation of α-deuteropolystyrene proceeds by a factor of 2 more slowly than the thermal degradation of normal polystyrene, the yield of monomer in the first case being 70 per cent and in the second 42 per cent. Since the replacement of the α-hydrogen atom by deuterium decreases the probability of isomerization, the relative yield of monomer by reaction (b) must increase. At the same time the resultant rate of the process must decrease. Consequently, the results in reference [8] also indicate the existence of isomerization reactions of radicals.

CONCLUSIONS

(1) The thermal kinetics of the thermal degradation of polypropylene have been studied in the temperature range 320–412°C. The effective energy of activation in the initial stage of the process of degradation is found to be equal to 55 kcal/mole.

(2) The phenomenon of inhibition of the thermal degradation of polypropylene by additions of 2,2-di-*p*-oxyphenylpropane has been discovered and it is shown that the reciprocal of the rate of degradation depends linearly on the quantity of inhibitor added.

(3) From the low value of the activation energy for the degradation process of polypropylene and from its inhibition law the conclusion is drawn that the process is of a chain nature.

(4) It is shown that the composition of the gaseous process can be explained by the existence of isomerization of aliphatic radicals formed in the degradation process.

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INVESTIGATION OF THE COMPATIBILITY OF POLYMERS—THE VISCOSITY OF SOLUTIONS OF NITROCELLULOSE AND POLYVINYLCHLORIDE AND OF THEIR MIXTURES WITH POLAR RUBBERS*

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THE investigation of the process of mutual solubility of polymers has much importance in the development of the theory of solutions, and for practical purposes.

Our series of reports, and also the work of other authors, established that as a result of successful combinations of one polymer with others, new materials are obtained with properties superior to those of straight polymers.

In our work [1], it was shown that on mixing nitrocellulose with butadiene-acrylonitrile rubber, compatible polymers were obtained with much better mechanical and physical properties than the original polymers. These combined polymers have been used in the manufacture of automobile and furniture upholstery instead of nitrocellulose plasticised with castor oil; an appreciable improvement in quality of these materials was obtained.

On combining polyvinylchloride and polyvinylacetate with butadienevinylydenechloride rubber [2], a polyamide with polyvinylacetate [3], and also nitrocellulose, polyvinylchloride and polyvinylacetate with carboxylated rubbers [4], compatible polymers were obtained. These polymers had better mechanical and machining properties than the parent polymers.

Zelikman and Mikhailov [5] show that a copolymer of vinyl chloride with acrylonitrile gives synthetic fibres with a better set of properties than the straight polymers.

Up to the present time, the mechanism of compatibility of polymers has been little studied and has not been fully solved. An explanation of the process would help us to choose pairs of compatible polymers which would give materials with required properties.

Different authors have proposed various methods of measuring the degree of compatibility of polymers, both with low molecular weight liquids and with each other.

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† L. P. Morina participated in the experimental work.

In this case we will consider only one of these—the measurement of the viscosity of solutions of polymers in low molecular weight plasticisers, and of various polymers in organic solvents—with a view to evaluating the interactions between them.

Frith [6] measured the specific viscosity of solutions of polyvinylacetate and polyvinylchloride in low molecular weight plasticisers. The relative compatibility of plasticisers with polymers was expressed as the slope of the curve of η_{sp} with respect to c (where η_{sp} is the specific viscosity; c is the % concentration of the solution). The author showed that when attractive forces exist between the mixed species the slope of the curve diminishes with an increase in temperature, and when these attractive forces are absent it increases. These conclusions have been confirmed by a series of other workers [7, 8] and also by the present work.

An increase in viscosity of mixtures of solutions of ethylcellulose with polyethyleneglycol has been found when compared with the additive values. The authors explained that this is due to the interaction between molecules of these substances.

It has also been shown that the initial slope of the curve (η_{sp} against c) can be used to estimate the interaction between a solvent and a polymer.

Mikhailov and Zelikman [10] measured the viscosity and the osmotic pressure of polyvinylchloride and polyacrylonitrile solutions in dimethylformamide. On the basis of their results, it is concluded that in a dimethylformamide solution polyvinylchloride has the form of spheres, while molecules of polyacrylonitrile are elongated.

On the basis of their data on the swelling of butadiene-styrene rubber in various plasticisers and data on the viscosity of dilute solutions of the rubber in the same plasticisers, Zubov and Zverev [11] made the assumption that the chain molecules of rubber have a more compact configuration in the presence of polar plasticisers (with which they are incompatible), than in the presence of non-polar plasticisers.

This shows the important effect that the polarity of polymers has on their compatibility. At the same time the presence of chemical interaction between the mixed substances is important. Thus, in accordance with [12], if two liquids with different viscosities do not react with each other on mixing, then the viscosity of the mixture has an intermediate value. The viscosity of a mixture of two liquids, which react on each other, is higher than that of the component liquids.

EXPERIMENTAL SECTION

On the basis of the results quoted above it follows that the measurement of viscosity of polymer solutions can give an indication of the compatibility of these polymers with each other.

We have applied these methods to other systems (mixtures of nitrocellulose and polyvinylchloride with polar rubbers), which so far have not been studied by other authors.

Viscosity of solutions of mixtures of nitrocellulose with butadieneacrylonitrile rubber. Viscosities of 0·2, 0·7 and 2% solutions of nitrocellulose, butadiene-acrylonitrile rubber (SKN-26) and their mixtures were measured at 20, 40 and 60°C. The proportions of the components in mixtures were 25:75; 50:50; and 75:25.

Viscosities were measured using an Ostwald-Pinkevich viscometer with a capillary 1mm in diameter. Redistilled ethyl acetate was used for the preparation of nitrocellulose solutions and a mixture of redistilled ethyl acetate and redistilled benzene, in the ratio 2:1, for the preparation of SKN-26 solutions.

Times of flow were measured both for solvents and solutions. The relative viscosity was calculated from the formula:

$$\eta_{rel} = \frac{\tau_1 d_1}{\tau_0 d_0}, \tag{1}$$

where τ_0 = time of flow of the solvent; d_0 = specific gravity of the solvent; τ_1 = time of flow of the solution; d_1 = specific gravity of the solution.

The results of these measurements are shown in Fig. 1. From this it can be seen that the relative viscosity of solutions of nitrocellulose, butadiene-acrylonit-

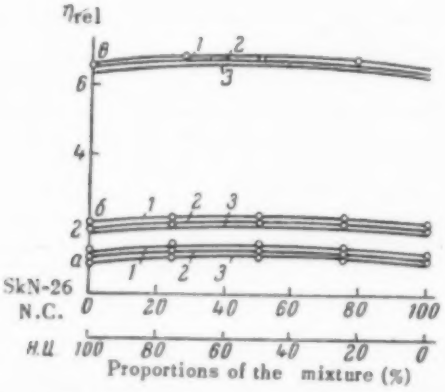

FIG. 1. Relative viscosity (η_{rel}) of solutions of nitrocellulose, rubber and their mixtures. (a) Concentration 0·2; (b) 0·7; (c) 2%; (1) Temperature 20°C; (2) 40°C; (3) 60°C.

rile rubber (SKN-26) and of their mixtures increases with an increase in concentration, but decreases with an increase in temperature.

The viscosity of solutions of nitrocellulose and rubber SKN-26, taken in different proportions, is higher than the additive values.

Viscosity of mixtures of solutions of Polyvinylchloride and polar rubbers. The viscosity of 2·5% *cyclo*hexanone solutions of polyvinylchloride, nairite NT, chloroprene rubber from low temperature polymerisation, butadiene-acrylonitrile rubber SKN-26, mixtures of rubbers and mixtures of polyvinylchloride with combinations of above rubbers, were measured at 20 and 50°C. *Cyclo*hexanone redistilled at 150°C was used for the preparation of these solutions.

The solutions were prepared by heating a weighed amount of finely ground polymer (in the case of polyvinylchloride—weighed amount of powder) with the solvent on a water bath under reflux for 4 hr.

Results of the viscosity measurements are shown in Fig. 2 and 3.

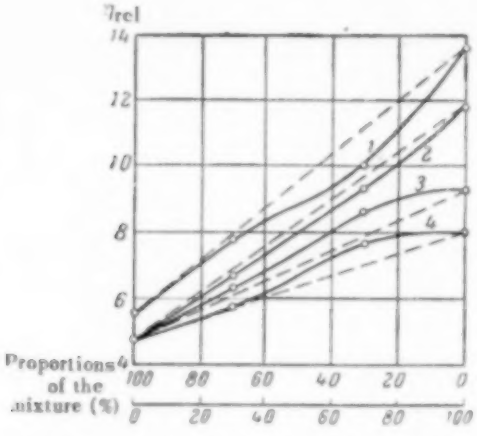

FIG. 2. Relative viscosity (η_{rel}) of 2·5% solutions of polyvinylchloride, nairite, SKN-26 and their mixtures in *cyclo*hexanone. (1) Solution of nairite and polyvinylchloride at 20°C; (2) The same at 50°C; (3) Solution of SKN-26 and polyvinylchloride at 20°C; (4) The same at 50°C.

From Fig. 2 it can be seen that of the polymer solutions studied, the nairite solution has the highest and the polyvinylchloride solution the lowest relative viscosity (η_{rel}).

Increase in temperature causes a lowering of the value of η_{rel}.

The viscosities of solutions of mixtures of polyvinylchloride with nairite are lower than the additive values, shown as dotted lines in Fig. 2.

The viscosities of mixtures of the polyvinylchloride and rubber SKN-26 solutions, and also those of the three component mixtures: polyvinylchloride, nairite and SKN-26 rubber, are higher than the additive values, shown as dotted lines in Fig. 3.

The first example indicates incompatibility of polyvinylchloride with nairite and compatibility is indicated in the remaining examples.

When solutions of compatible polymers are mixed, complexes are formed, by the association of the different macro-molecules in solution. These associated molecules have an elongated configuration. As the result of this, the time of flow of the mixtures through the viscometer capillary increases and therefore the viscosity of the solution increases. This is found experimentally with a mixture

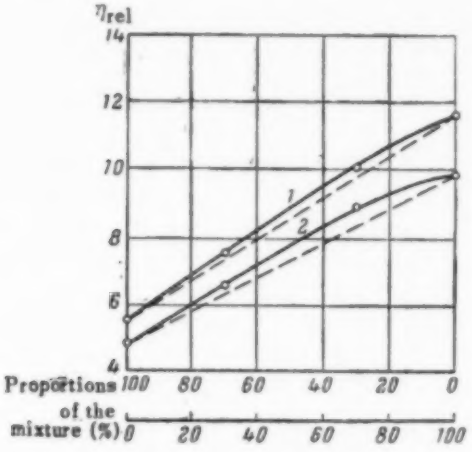

FIG. 3. Relative viscosity (η_{rel}) of 2·5% *cyclo*-hexanone solutions of polyvinylchoride and of mixtures with combinations of nairite and rubber SKN-26. (1) Nairite + SKN-26 + polyvinylchloride at 20°C; (2) The same at 50°C.

of nitrocellulose and butadiene-acrylonitrile rubber(containing 20% of acrylonitrile groups), with mixtures of polyvinylchloride and butadiene-acrylonitrile rubber and also with the three component mixtures of polyvinylchloride, butadiene-acrylonitrile rubber and nairite.

When non-compatible or partially compatible polymers are mixed, the molecular configuration of the polymers becomes more compact. The time of flow of the mixtures of solutions of such polymers through the viscometer capillary decreases and consequently the viscosity decreases. This is found to be true with mixtures of polyvinylchloride and nairite which are compatible only to a limited extent.

To explain the results of these tests we tabulated the values of the dielectric constants (ε) of the polymers and solvents studied:

TABLE 1. VALUES OF DIELECTRIC CONSTANT OF SOME COMPOUNDS

Name of the polymer or the solvent	ε (at 20°C)
Butadiene-acrylonitrile rubber (SKN-26).	10·5
Nitrocellulose	7·8
Ethyl acetate	6·4
Benzene	2·3
Polyvinylchloride	3·5
Nairite	5·0
*Cyclo*hexanone	18·2
Ethyl alcohol	24·3

From the above data it can be seen that the dielectric constants of butadiene-acrylonitrile rubber and nitrocellulose are of similar magnitude, while the dielectric constants of butadiene-acrylonitrile rubber and polyvinylchloride are different. The dielectric constants of the *cyclo*hexanone solutions of these substances, however, are similar since the solutions are of low concentration and the dielectric constant of *cyclo*hexanone is the dominating factor.

Polyvinylchloride is miscible with butadiene-acrylonitrile rubber in the absence of a solvent at 140–150°C. Under these conditions the dielectric constant of polyvinylchloride increases to 12 [13]; and that of the rubber SKN-26 remains approximately constant, so that the values for these two polymers are almost identical. In the case of polyvinylchloride mixed with a combination of butadiene-acrylonitrile rubber and nairite, the dielectric constants of both components are also of similar magnitude.*

On the basis of the above data, it was assumed that polymers which are compatible with each other or with their combinations, have similar dielectric constant values, while non-compatible polymers have somewhat differing values. In addition, the density of packing of the molecules of polymers and solvents, the thermodynamic properties and the chemical structure of the polymers also play their part.

CONCLUSIONS

(1) The viscosity of solutions of nitrocellulose, butadiene-acrylonitrile rubber and their mixtures in different proportions were measured at 0·2, 0·7 and 2% concentration and at 20, 40 and 60°C.

* In the case of the miscibility of polyvinylchloride with nairite, which occurs in the absence of a solvent at 150°C, the dielectric constant (ε) of polyvinylchloride increases from 3·5 to 12 and that, of nairite has an approximately constant value of 6. Thus the difference in the values of (ε) in this case is appreciable.

An increase in viscosity of solutions of mixtures of these polymers has been found in comparison with the additive values.

(2) The viscosity of 2·5% solutions of polyvinylchloride, butadiene-acrylonitrile rubber and mixtures of polyvinylchloride with the indicated rubbers and their combinations has been measured at 20 and 50°C.

An increase in viscosity of mixtures of solutions of polyvinylchloride with butadiene-acrylonitrile rubber and also of polyvinylchloride with a combination of butadiene-acrylonitrile rubber and nairite has been found, in comparison with the additive values. For solutions of mixtures of nairite and polyvinylchloride a decrease in viscosity, when compared with the additive values, has been found.

(3) The indicated positive and negative deviations of viscosities from the additive values can be explained by the fact that in the first case the polymers have practically the same, and in the second case different, polar properties. At the same time both the thermodynamic properties of polymers and other properties have an important effect.

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PREPARATION OF GRAFT COPOLYMERS—V. GRAFTING OF VINYL MONOMERS ON POLYETHYLENE *TERE*PHTHALATE (LAVSAN)*

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IN the present investigation the conditions for the synthesis of graft copolymers, from industrial materials was studied, using ozone as an activator for the polymerization. As the subject of our study we used a polyester—polyethylene *tere*phthalate ("lavsan"), used in the form of thin films and fibres.

As with polyamides, the initial samples of polyesters were treated with ozone and then heated in a stream of nitrogen, with styrene, acrylonitrile, vinylydene chloride and vinyl acetate. The method used has been described previously [1–3].

DISCUSSION OF RESULTS

The investigation showed a distinct possibility of applying the given method of grafting not only to the series of polyamides, but also to a series of polyesters. It was found that styrene easily grafts on to the polymer giving a graft copolymer with a conversion of up to 60 per cent. Moreover, films and fibres of lavsan, even without activation with ozone, react with styrene giving a graft copolymer but with a lower conversion.

A similar phenomenon, was observed earlier with a series of polyamides when samples reacted with vinyl monomers without being ozonised [3]. As we have shown in the study of polyamides, this reaction takes place with samples of industrial products in which active centres occur. The formation of the latter is caused by various factors—destructive oxidation, presence of impurities, etc—as a result of which peroxide and hydroperoxide groups are formed in the polymer.

Table 1 shows the change in weight of sample films of lavsan after copolymerization with styrene; Table 2—the same data shown for fibre samples of "lavsan".

Examination of these Tables shows that the yield of graft copolymers varies little with different samples of films.

* Vysokomol. soedin. **1**: No. 11, 1604–1609, 1959.

TABLE 1. GRAFTING OF STYRENE ON TO LAVSAN FILMS (5 HR AT 80°C IN A STREAM OF NITROGEN)

Ozonization		Increase in weight after grafting (%)
Time (min)	Increase in weight (%)	
0	—	46·79
5	1·04	43·76
10	—	52·61
60	0·78	52·84

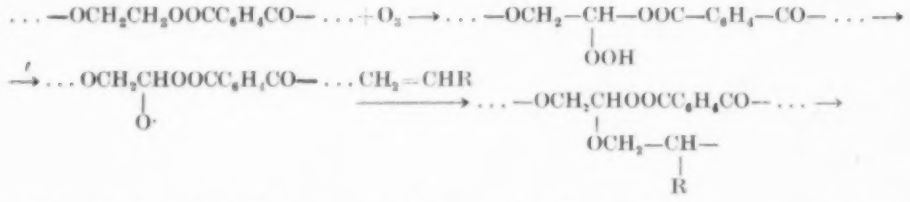
TABLE 2. GRAFTING OF STYRENE ON TO LAVSAN FIBRES (5 HR AT 80°C IN A STREAM OF NITROGEN)

Ozonization		Increase in weight after grafting (%)
Time (min)	Increase in weight (%)	
0	—	17·01
5	0·39	23·38
10	0·25	39·81

Comparing these results with the data found for the fibres, it can be seen that for the latter the yield of the copolymer is lower than that for the films. These facts agree with the observations made by us on a series of polyamides, and they are apparently explained by the different degree of orientation of films and fibres and the resultant opportunity for the materials to absorb the monomer.

We suggest that the interaction of the ozonised polyester with the vinyl monomer occurs as the result of the formation of a hydroperoxide, which decomposes to give a free radical, which then initiates the polymerization.

We think that the graft polymer based on lavsan and styrene is formed by the following mechanism:



It is obvious that this process of formation of a graft polymer may not develop in such a simple way as that indicated by the above mechanism. It is possible that other parallel reactions occur simultaneously.

In Table 3 are given the changes found on testing the mechanical properties of the original films of lavsan and films after grafting on of styrene.

Analysis of the above data leads us to the conclusion that if the sample of polyester is ozonised for a short time (5 min) then its elongation increases as a result of copolymerization with styrene, although its stability towards breaking decreases. The copolymer obtained from prolonged ozonisation of the sample, becomes more brittle (elongation decreases), possibly on account of the growth of a layer of polystyrene, and the resistance to breaking increases slightly (apparently, as a result of linking of the polymer chains under the influence of ozone).

TABLE 3. CHANGE IN MECHANICAL PROPERTIES OF FILM AND FIBRE SAMPLES OF LAVSAN, AFTER OZONIZATION AND GRAFTING ON OF STYRENES

Form of material	Original sample		Time of ozonization (min)	The same sample after ozonization and grafting of styrene	
	%	kg/cm²		%	kg/cm²
Film	192·7	1552	5	280	876·4
Film	192·7	1552	300	192·1	1115·0
Fibre	16·6	5852	5	31	4018

Measurement of the film thickness of the samples before and after grafting showed that it increased from 19–20 μ for the initial samples to 32–38 μ for the final samples.

During the study of the thermo-chemical properties of lavsan it was found that, after the grafting on of styrene, it began to melt at a higher temperature, although this increase is not so marked as in the case of amide G-669 and styrene (Fig. 1).

The data in Table 4 show that with an increase in the time of ozonization the viscosity of lavsan solution gradually increased, which is explained by the

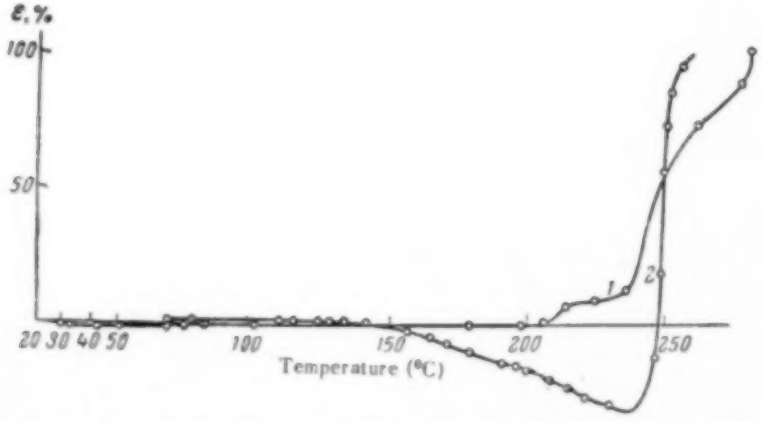


FIG. 1. Thermo-mechanical curves of samples of lavsan films. (1) Initial sample; (2) After treatment with styrene.

cross-linking of chains under the influence of ozone. After the treatment of the ozonised sample with styrene the specific viscosity of its solutions became even higher, apparently as the result of formation of new chains, probably much longer, partially branched and even cross-linked.

TABLE 4. CHANGE IN VISCOSITY OF 0·5% SOLUTION OF SAMPLE IN CRESOL AFTER OZONIZING AND GRAFTING ON OF STYRENE (5 HR AT 80°C IN A STREAM OF NITROGEN)

η_{sp} before ozonization	η_{sp} after copolymerization without ozonizing	Time of ozonizing: 5 min		Times of ozonizing: 5 hr	
		η_{sp} after ozonizing	η_{sp} after copolymerization	η_{sp} after ozonizing	η_{sp} after copolymerization
0·248*	—	0·273	0·464	0·305	0·610
0·272†	0·705	—	0·742	—	—

* Viscosity measured in 1957; solvent – *m* – cresol. † Viscosity measured in 1959; solvent tri-cresol.

Grafting of polystyrene on to samples of lavsan which occurred with a noticeable absorption, was found to change the elementary structure of the original polyester.

Table 5 shows the change in the elementary structure of the grafted samples compared with the original: after grafting of styrene a noticeable increase of the carbon content (up to 10 per cent) and hydrogen content is observed in the samples.

Growth of a surface layer of polystyrene on the polyester not surprisingly altered the ease with which the grafted polymers are wetted by various solvents. A noticeable decrease in wetting of the samples by solvents such as benzene, chloroform and dioxane was discovered.

TABLE 5. CHANGE IN THE ELEMENTAL ANALYSIS OF FILM AND FIBRES OF LAVSAN BEFORE AND AFTER OZONIZING AND TREATMENT WITH STYRENE

Form of material	Composition of original sample (%)		Time of ozonizing (min)	Composition of grafting Copolymer (%)		Calculated for $(C_{10}H_8O_4)$ (%)	
	C	H		C	H	C	H
Fibre	62·13	4·18	5	68·29	5·01	62·50	4·19
	61·95	4·19		68·30	4·99	—	—
Fibre	61·95	4·19	10	71·47	5·40	—	—
				71·72	5·43	—	—
Film	62·52	4·30	60	73·11	5·45	—	—
	62·53	4·48		72·87	5·47	—	—

The study of the optical properties of film samples showed that the infra-red spectra of graft polymers differ from the spectra of the original samples by changes in the region of 705 and 765 cm^{-1}.

Appearance of new absorption maxima at these wavelengths is evidence that the polyester acquires frequencies which are characteristic of the mono-substituted benzene derivatives. From the data of Bellamy [4], these frequencies

represent the non-planar deformation vibrations of the C—H bonds. The I.R. absorption spectra are shown on Fig. 2a, b and c.

Study of the same samples in the U.V. region of spectrum shows a certain difference caused by the grafting of polystyrene; the absorption curve for lavsan

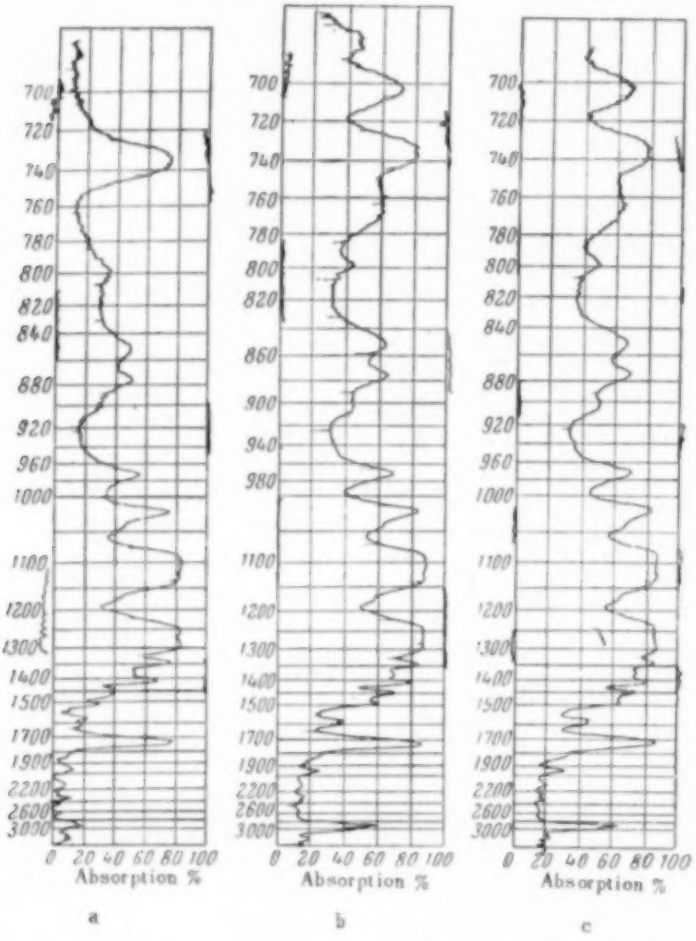


FIG. 2. Infra-red absorption spectra. (a) Initial sample of lavsan film; (b) The same sample after treatment with styrene, without ozonisation; (c) After treatment with styrene with preliminary ozonisation for 10 min.

is however very indistinct and therefore these changes are insufficiently characteristic. Changes in U.V. absorption of the samples is shown in Fig. 3a and 3b.

The ease of grafting of other monomers on to ozonised samples of lavsan was studied for the fibres of this polyester and such monomers as vinyl acetate

and vinylidene chloride. It was found that both monomers graft on to the fibres very weakly; this is in agreement with our observations on the interaction of

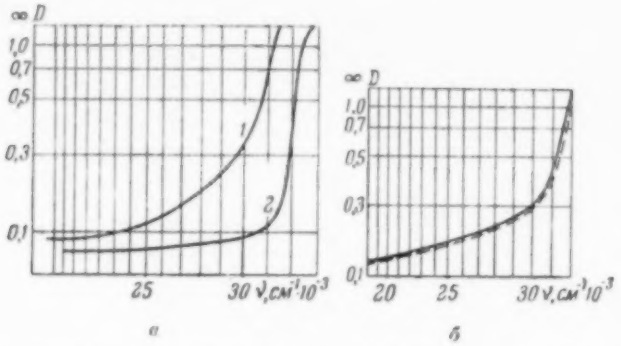


FIG. 3. Ultra-violet absorption spectrum. (a) Initial sample of lavsan film; (b) The same sample after treatment with styrene: (1) without ozonising; (2) sample previously ozonised for 10 min.

TABLE 6. TREATMENT OF LAVSAN FIBRES WITH VINYLIDENE CHLORIDE (5 HR AT 30°C IN A STREAM OF N_2)

Ozonization		Increase in weight after grafting (%)
Time (min)	Increase in weight (%)	
0	—	1·78
5	0·39	0·93
300	2·09	None

TABLE 7. TREATMENT OF LAVSAN FIBRE WITH VINYL ACETATE (5 HR AT 75°C IN A STREAM OF N_2)

Ozonization		Increase in weight after grafting (%)
Time (min)	Increase in weight (%)	
0	—	1·94
5	0·18	1·31
30	—	3·00
300	2·05	None

these monomers with polyamides [3]. The experimental results obtained are given in Tables 6 and 7.

On studying the same reaction with acrylonitrile it was found that the latter can graft on to the fibre, giving a weight increase of up to 84 per cent. This increase in weight was obtained with samples ozonised for not less than an hour, and this indicates that this monomer needs a larger number of "active" centres for effective copolymerization than was found earlier when its grafting on to caprolactam fibre was examined.

EXPERIMENTAL SECTION *

For the purpose of the investigation, manufactured fibres and films of lavsan were used. The latter had a thickness of 0·20 to 0·40 μ. The method of work was the same as that used earlier. The final samples were boiled in benzene, washed in the same solvent and dried to constant weight at 55–60°C.

Samples (0·2000–0·3000 g) were treated with ozone, heated with styrene in a stream of purified nitrogen at 80°C, then boiled in benzene and dried to constant weight. The change of properties was established by measuring the increase in weight, change in mechanical, thermochemical and optical properties, viscosity, elemental analysis etc.

The authors express their gratitude to I.V. Obreimov, G.L. Slonimskii and L.Z. Rogovina for help in carrying out mechanical and optical studies on the samples.

CONCLUSIONS

(1) In the case of polyethyleneterephthalate (lavsan) and vinyl monomers the possibility of obtaining graft copolymers from polyesters was observed, using ozone to initiate the polymerization.

(2) A mechanism for the reaction of grafting vinyl monomers on to polyethylene*tere*phthalate has been proposed.

(3) The data, obtained earlier on polyamides, has confirmed that the yield of graft copolymer depends on the degree of orientation in the material under consideration.

(4) It was found that of the vinyl monomers studied, styrene gives the highest yields of the graft copolymer.

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* Zasechkina and Volkova participated in the experimental work.

ULTRASONIC DEGRADATION OF POLYACRYLONITRILE SOLUTIONS*

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AMONG the many new methods of synthesizing high molecular weight substances developed during the last few years, an appreciable number are mechanochemical processes. Intensive mastication of various types of polymers enables us to obtain very interesting new forms of polymeric materials of the block copolymer type. Recombination of macromolecules, occurring during the breakdown of polymer molecules leads to the formation of new substances, which are difficult to obtain by normal chemical methods. Occurrence of the breakdown processes is mainly determined by two factors: reactivity of the macroradical and the mobility of the hydrogen atom taking part in the chain transfer reaction [1]. Breakdown processes can obviously be carried out not only in the solid but also in the liquid phase, for example in solution under the action of ultrasonic waves.

It was found some time ago [2] that the solution viscosity of such natural polymers as rubber latex, agar-agar, gelatine, starch, etc., decreases under the action of ultrasonic waves. This effect was apparently caused both by the degradation of the solutions and by depolymerization of the naturally occurring high molecular weight substances. Later the processes of ultrasonic depolymerization of various natural and synthetic materials were studied in detail by a number of authors [3].

To be able to choose correctly the conditions for compatible degradation of various types of polymers which would then recombine completely to form new block-copolymer materials, it is necessary to study the process of degradation of individual polymers. The true process of degradation of dissolved polymers can be studied easily in sufficiently dilute solutions, for which it is not necessary to consider the energy of interaction between the macromolecules. From this point of view the work of Schmid and co-workers who studied the change in prop-

* Vysokomol. soedin. **1**: No. 11, 1610–1616, 1959.

erties of carbon chain and mixed chain polymer solutions under the action of ultrasonic waves [4] offers considerable interest. It was shown that the viscosity of dilute solutions of polymers, and therefore the molecular weight, decreases irreversibly, and the kinetics of the breakdown of macromolecules are described by the following equation:

$$\frac{dx}{dt} = kN_L(P - P_e)$$

where x=number of bonds broken by the action of the ultrasonic waves per unit volume at a given time t; P=degree of polymerisation at the time t; P_e=final degree of polymerisation; N_L=Loschmidt's number; k=a constant. Shmid's equation agrees well with experimental data.

However, treatment of the mechanism of depolymerization as a consequence of the action of large frictional forces between molecules of the solvent and the polymer chains, developed in the ultrasonic field, does not appear convincing. It is necessary to note that numerous works of other authors [5] show the error of Schmid's assertion that cavitation plays no part in depolymerization by an ultrasonic field.

During the degradation of high molecular weight substances by the action of ultrasonic waves, the original fractional composition of the polymer can change. While studying the process of ultrasonic degradation of polymer chains in solution, on the example of benzene solutions of polystyrene, Jellinek and White [6] showed that the molecular distribution of the polymer changed under the action of ultrasonic waves of 500 kc frequency for times ranging from 0·5 to 9 hr. An analysis of the experimental material, of various workers on the influence of ultrasonic waves on polymer solutions, shows that the process occurs by a molecular mechanism. Cerf and Mayer [7] showed that for α-benzene solutions of polystyrene the coefficient of absorption of the ultrasonic waves, α, depends on the molecular weight. For the sample of polystyrene with molecular weight of 400,000, the characteristic coefficient of absorption is 12 c.g.s. units. Wada and Yamamoto [8] point out the molecular mechanism of the action of ultrasonic waves on polymers.

Of all the polymeric materials, used at present time for the manufacture of chemical fibres, polyacrylonitrile is of most interest. However, the comparatively high brittleness of articles made from this material and its bad dye retention with common dyes, makes the problem of modifying the properties of this polymer very urgent.

The method of compatible ultrasonic depolymerization of various polymers is interesting for the synthesis of new block copolymers. In the present work, the authors have tackled the problem of studying the process of degradation of polyacrylonitrile (PAN), dissolved in dimethylformamide (DMF) (with the polymer concentration of 5 g/l.) under the influence of an ultrasonic field.

EXPERIMENTAL SECTION *

The PAN used was obtained by polymerizing acrylonitrile in an aqueous solution by applying an oxidation-reduction initiator [9]. The specific gravity of the polymer was 1·14 g/cm³, ash = 0·06 per cent, and the specific viscosity of 0·5% solution of PAN in DMF was 1·780. DMF was used as a solvent (d_4^{20} = = 0·949; b. pt. = 152·5°C; n_D^{25} = 1·4269), the physico-chemical properties of which and the effect of ultrasonic waves on it in a wide temperature range have been described by us in detail [10].

The observations were made in the range of concentrations from 1 to 5 g/l., since in more concentrated solutions in DMF, PAN begins to show signs of abnormal viscosity.

The irradiation of solutions was carried out by using an ultrasonic generator of the type G.U.-3, made by MosKIP, in the range of frequencies from 350 to 750 kc with output energy up to 20 W/cm². The energy of radiation was controlled by the magnitude of the grid current, the anode potential and the filament current of the generating valve G.U.-80.

The kinetics of the depolymerization were studied at 25–60°C; to decrease the temperature variations during "sounding" of solutions, the reaction vessel was enclosed in a thermostat. The degree of depolymerization was estimated from the characteristic viscosity $[\eta]$. Viscosity was measured in an Ostwald-Pinkevich viscometer at $25 \pm 0{\cdot}1$°C. The molecular distribution of PAN was studied by the method of fractional precipitation with turpentine from solutions in DMF, with subsequent reprecipitation of the resulting polymer fractions in acidified water. On the basis of the experimental data thus obtained an integral curve was plotted, from which, using the method of graphical differentiation, the differential $[\eta]$ distribution curve was obtained.

For control, and to suppress the possibility of oxidation-reduction reactions occurring during the irradiation of the PAN solutions, an indicator method was used. A 0·1 N solution of I_2 was used as an indicator. As experiments showed, the iodine titration of a pure DMF and of a solution of PAN in DMF with a concentration of 5 g/l. does not change at 25°C during a period of 5 weeks. The iodine titration also remained constant on prolonged irradiation (up to 3 hr), if the temperature of the process does not exceed 70°C. At higher temperatures a decrease in iodine consumption was noted, probably as the result of evaporation. After a large number of experiments, the following experimental procedure was chosen for the study of the degradation process: 15 min of irradiation with 15 min intervals.

Moreover, measurements of the speed of the ultrasonic waves in solution were made, before and after irradiation. The speed of propagation of ultrasonic waves was measured in a vessel of optical glass; the diffraction maxima were

* Kulikova and Volkova participated in the experimental work.

counted by means of a special screw micrometer, and the measurement of frequency with a heterodyne wavemeter. The speed of the ultrasonic waves was measured at the fundamental frequency (3 mc) and on the third harmonic (9 mc); the relative error of the measurement did not exceed 0·3 per cent. On the basis of the data obtained from the measurements of the speed of propagation of ultrasonic waves, the adiabatic compressibility was calculated from the usual hydrodynamic formula:

$$\beta = 1/c^2\rho ,$$

where c=speed of the ultrasonic waves; ρ=density of solution, determined by the dilatometric method, which ensured a precision of $\pm 3 \times 10^{-4}$ g/cm^3.

The experimental results obtained are showed in Fig. 1–6.

DISCUSSION OF RESULTS

The speed of propagation of ultrasonic waves in solutions of polymeric substances obviously depends on a number of factors: the chemical nature of the solvent and of the dissolved substance, the energy of interaction between molecules of solvent and polymer, solvation, etc. DMF is extremely polar, highly dissociated liquid, and is characterized besides by an appreciable similarity to PAN. The value of the total heat of solution of PAN in DMF is 8·1 cal/g. Clearly the speed of propagation of ultrasonic waves in dilute solutions should not differ appreciably from the speed in the pure solvent.

In Fig. 1 our experimental data is given, which shows that the speed of the ultrasonic waves, c, decreases linearly with an increase in temperature from

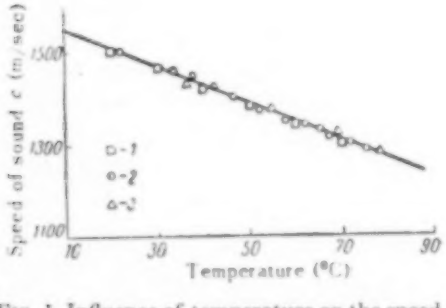

FIG. 1. Influence of temperature on the speed of ultrasonic waves in DMF and in dilute solutions of PAN. (1) Pure DMF; (2) Unsounded 0·5% solution of PAN; (3) Sounded solution of PAN.

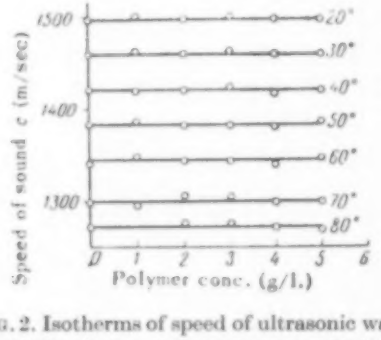

FIG. 2. Isotherms of speed of ultrasonic waves in PAN solutions of various concentrations.

20 to 90°C. Any differences that there are in the speed of the ultrasonic waves in the pure solvent and in solution with a PAN concentration of 5 g/l. were not discovered (Fig. 2). Calculation of the adiabatic compressibility β on the

basis of data on the speed of ultrasonic waves and density of solutions (Fig. 3) confirm the assumption that in dilute solutions the influence of the polymer on the speed of propagation of ultrasonic waves and on the change of energetic characteristics of the solution is comparatively small. At low energy density observations (up to 0·5–1 W/cm²) and also at high frequencies up to 9 mc, noticeable changes in properties of solutions were not observed. However, on applying a dense (up to 20 W/cm²) ultrasonic field, degradation of polymer chains was observed. As can be seen in Fig. 4, on applying dense radiation to a solution of PAN an appreciable decrease in viscosity was observed. This cannot have been caused by disentanglement of macromolecules, since in dilute solutions, the proportion of associated compounds is negligible. Thus the decrease in viscosity is an irreversible process, probably caused only by the breakdown of polymer chains. No additional changes in viscosity of irradiated solutions was observed even after 5 weeks storage. As is seen in Fig. 4, the degree of decrease in viscosity after the same length of time of irradiation is smaller at lower concentrations. This is in agreement with the experimental results of Schmid

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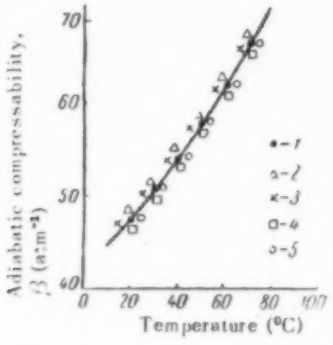

FIG. 3. Adiabatic compressibility of solutions of PAN in DMF at low polymer concentrations. (1) Pure DMF; (2) 0·1% PAN solution; (3) 0·2% PAN solution; (4) 0·3% PAN solution; (5) 0·5% PAN solution.

and Rommel, [11], obtained on solutions of polystyrene in toluene. From the results of kinetic observations a graph of the dependence of $[\eta]$ on t (Fig. 5) was made. The most probable form of the process of degradation of PAN in DMF was calculated by statistical methods, in the same way as was done by Laufer and Price in their work on the kinetics of the thermal degradation of the albumin in the tobacco mosaic virus, [12]. The breakdown of the polymer molecules occurs formally by a reaction of the 1st order.

If the rate of decrease of the characteristic viscosity is defined as:

$$v = \frac{d\{[\eta]_t - [\eta]_\infty\}}{dt},$$

then clearly:

$$v = -k\{[\eta]_t - [\eta_\infty]\} \ldots \quad (1)$$

Integration and putting the limits in the equation (1) lead to the following form:

$$[\eta]_t = \{[\eta]_0 - [\eta]_\infty\} e^{-kt} + [\eta]_\infty \cdots \quad (2)$$

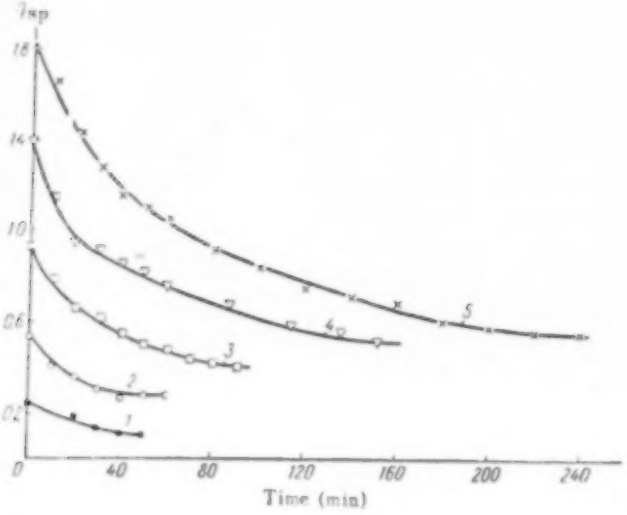

FIG. 4. Kinetics of the decrease in viscosity of dilute PAN solutions at frequency of 0·5 mc. (1) 0·1%, (2) 0·2%, (3) 0·3%, (4) 0·4%, (5) 0·5%.

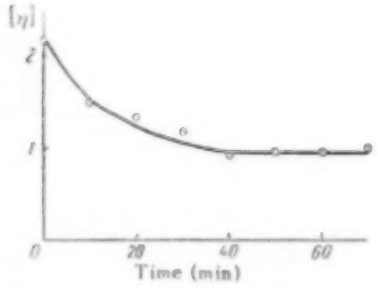

FIG. 5. Kinetics of depolymerization of PAN at a frequency of 0·5 mc.
Vertical scale: $[\eta]$; Horizontal scale: Time, min.

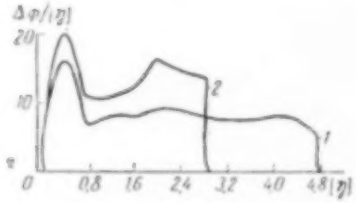

FIG. 6. Change in the molecular distribution of PAN as the result of sounding. (1) Differential curve of distribution before sounding. (2) The same after sounding at a frequency of 0·5 mc.

Here $[\eta]_0$ = characteristic viscosity of solution before "sounding", $[\eta]_t$ = characteristic viscosity of solution after t min of irradiation, $[\eta]_\infty$ = characteristic viscosity after achieving equilibrium.

A check showed that the proposed formula agrees with the experimental data.

Obviously equation (2) can be converted into Schmid's equation by appropriate substitutions.

The velocity constant for the process, calculated by the usual methods, is equal to $2{\cdot}5 \times 10^{-2}\,\text{min}^{-1}$. It is interesting to note that in a recent work by Baramboim [13], on the kinetics of the degradation mechanism of various carbon chain polymers during intensive mastication, constants of similar order are given. This enables us to assume that in the process of ultrasonic depolymerization of PAN, the essential part is brought about by purely mechanical factors (cavitation, etc.).

In the process of ultrasonic degradation appreciable changes occur in the molecular distribution of PAN. In Fig. 6, differential curves are shown, of the distribution of molecular weights in the "unsounded" and "sounded" polymer. These results simply show that under the action of the ultrasonic field, degradation occurs mainly to the long macromolecules. Apparently the energetic stability of the macromolecules plays an essential part in the process of ultrasonic depolymerization. Narrowing of the molecular weight distribution band under the action of the ultrasonic field can probably be utilised to "ennoble" dissolved or molten polymers, since it is a known fact that a narrow distribution of molecular weight in a polymer will result in a material which has superior utilitarian properties.

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Our experiments on ultrasonic degradation of dissolved PAN were made under conditions which excluded the possibility of sporadic chemical processes. Clearly, heating solutions of PAN in DMF to 80–90°C does not lead to any changes in the properties of the polymer and the solvent; further increase in temperature causes yellowing and later gelling of the solutions. The darkening of the solutions is caused by the change in the nature of the side chains in the polymer, but not by the breakdown of the macromolecules.

Even prolonged heating of PAN at 150–180°C does not lead to any depolymerization. It can be assumed that during the ultrasonic degradation spots of local overheating are possible, but this discontinuity would have led to a change in the optical density of solutions. However, photocolorimetric study of the solutions, before and after irradiation, showed that no noticable change in the chemical nature of the polymer was obserwed. Experiments on the chemical indication of the process using iodine solution, fully confirmed the results of the optical measurements.

From the experimental data obtained it is clear that the lowering of the molecular weight of the polymer tends to a certain constant value, determined by the conditions of the experiment. Stabilization of the molecular weight during the degradation of the polymer in solution is apparently determined by both the mobility of the α-hydrogen atoms, of the acrylonitrile segments participating in the chain transfer reaction, and the reactivity of the solvent molecules, which stabilize the depolymerizing macromolecule.

CONCLUSIONS

(1) The kinetics of depolymerization of polyacrylonitrile in dimethylformamide solution were studied. It was established that the degradation of the polymer occurs by a 1st order reaction. A hypothesis about the mechanism of the process was formed.

(2) The speed of propagation of ultrasonic waves in dilute solutions of polyacrylonitrile is almost independent of the concentration of the polymer over a wide temperature range.

(3) It was shown that during the process of ultrasonic depolymerization "ennobling" of the polymer occurs, which leads to the formation of a product with a more even molecular weight.

Translated by Z. KOWSZUN

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STUDIES OF FREE RADICAL REACTIONS IN IRRADIATED POLYTETRAFLUOROETHYLENE—II. DETERMINATION OF THE RATE CONSTANT OF THE REACTIONS $\dot{R}O_2 \rightarrow \dot{R} + O_2$ AND $\dot{R} + O_2 \rightarrow \dot{R}O_2$*

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IT is known that in polytetrafluoroethylene (teflon) under the influence of ionizing radiation there is formed the stable fluoroalkyl radical $\sim CF_2-\dot{C}F-CF_2\sim$, hereinafter denoted by $\dot{R}$. In the presence of oxygen this radical is converted into a peroxide radical: $\sim CF_2-CF(O\dot{O})-CF_2\sim$, which we shall denote by $\dot{R}O_2$.

The kinetics of the addition of O_2 cannot be studied directly since the reaction goes very rapidly (as will be shown below, the time for this reaction is 20 sec at room temperature). The limiting step in this case is the diffusion of oxygen into the sample, which has been used by us to investigate the diffusion characteristics of teflon [1]. Hence, in order to obtain data relating directly to the kinetics of the interconversion of the radicals, we studied the equilibrium between the radicals and the reverse reaction of the decomposition of the peroxide radical, which, at not very high temperatures, goes more slowly than the diffusion of oxygen from the sample.

STUDY OF THE EQUILIBRIUM $\dot{R}O_2 \rightleftarrows \dot{R} + O_2$

At atmospheric pressure and room temperature the equilibrium $RO_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} \dot{R} + O_2$ is shifted completely to the left and only the signal from the peroxide radical is observed. At high temperatures (240–300°), the equilibrium is shifted to the right to such an extent that we can record EPR signals from both radicals. However, at such high temperatures, close to the melting point of teflon ($\sim$320°), irreversible changes apparently take place in the sample—in particular, a destruction of the radicals which prevents the study of the equilibrium in pure form. Consequently, we carried out experiments at low pressures at which both radicals may be observed simultaneously in the equilibrium at lower temperatures (160–250°).

*Vysokomol. soedin. **1**: No. 11, 1634–1642, 1959.

The experimental procedure has been described in a previous communication [1]. In order to facilitate the more rapid establishment of the equilibrium, the sample was made in the form of a stack of leaves each with a thickness of 0·25 mm, and the dependence of the equilibrium on the temperature was studied at low temperatures. In this case, the time to establish the equilibrium was determined by the time for the addition of the oxygen, which is extremely small, and the time for the diffusion of the oxygen, which, for 0·25 mm leaves, is 100 sec at 150° [1].

In the experiment we measured the magnitudes I_α and I_β, where I_α is the maximum derived electron paramagnetic resonance signal from the peroxide radical and I_β is the maximum derived highest-intensity component of the signal from the fluoroalkyl radical. As has been shown in [1], the concentrations of the radicals may be expressed in relative, but identical, units if one takes into account the fact that

$$\frac{[\dot{\mathrm{R}}\mathrm{O}_2]}{[\dot{\mathrm{R}}]} = \frac{I_\alpha}{\beta \cdot I_\beta},$$

where $\beta = 0{\cdot}41\, e^{\frac{1500}{RT}}$.

The constant of the equilibrium under investigation is:

$$K = K^\circ e^{\frac{Q}{RT}} = \frac{[\dot{\mathrm{R}}\mathrm{O}_2]}{[\dot{\mathrm{R}}][\mathrm{O}_2]_p},$$

where Q is the heat effect of the reaction and $[\mathrm{O}_2]_p$ is the concentration of the oxygen dissolved in the sample, and, consequently:

$$\frac{I_\alpha}{I_\beta} = \beta \frac{[\dot{\mathrm{R}}\mathrm{O}_2]}{[\dot{\mathrm{R}}]} = \beta K \cdot [\mathrm{O}_2]_p.$$

On the other hand, from Henry's law:

$$[\mathrm{O}_2]_p = k_p \cdot p_{\mathrm{O}_2},$$

where p_{O_2} is the partial pressure of oxygen above the sample and k_p is the solubility constant, which is written in the form:

$$k_p = k_p^\circ e^{\frac{\Delta H_p}{RT}}.$$

Hence, finally

$$\frac{I_\alpha}{I_\beta} = \beta K \cdot k_p \cdot p_{\mathrm{O}_2} = \beta^\circ \cdot K^\circ \cdot k_p^\circ \cdot p_{\mathrm{O}_2} \cdot \exp\left\{\frac{Q + \Delta H_p + \varepsilon_\beta}{RT}\right\},$$

whence

$$\log \frac{I_\alpha}{I_\beta} = \log (\beta^\circ \cdot K^\circ \cdot k_p^\circ \cdot p_{\mathrm{O}_2}) + \frac{Q + \Delta H_p + \varepsilon_\beta}{2{\cdot}3\, RT}.$$

Figure 1 shows the dependence of the experimental magnitude of $\log I_\alpha/I_\beta$ on the reciprocal of the temperature. With the exception of those at very small pressures (0·4 mm and below), the experimental points lie well on a straight line. At small pressures and temperatures below 130° we did not observe the

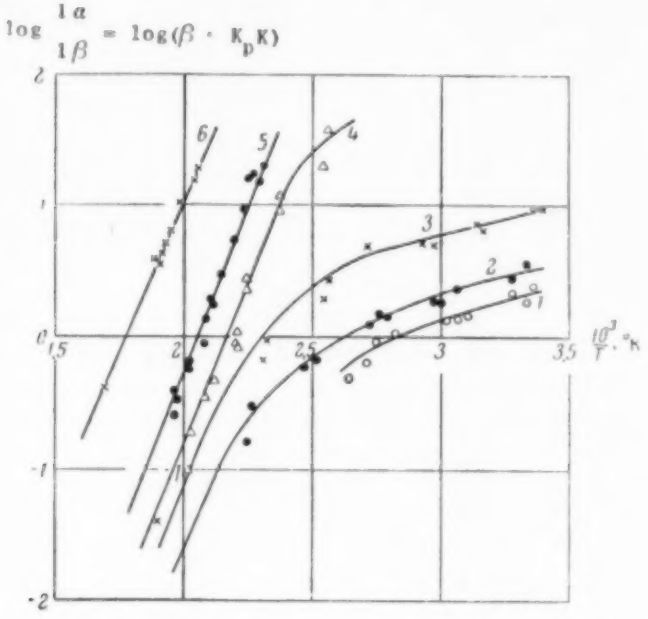

FIG. 1. Temperature dependence of the equilibrium $\dot{R}O_2 \rightleftarrows \dot{R} + O_2$ at various pressures (p_{O_2})
1 – 0·02 mm; 2 – 0·06 mm; 3 – 0·2 mm; 4 – 0·4 mm; 5 – 12 mm; 6 – 20 mm.

establishment of equilibrium in the time of an experiment ($\sim$10 min). This is connected, apparently, with the fact that at these low concentrations of dissolved

TABLE 1. RESULTS OF CALCULATIONS OF THE EQUILIBRIUM FROM THE EXPERIMENTAL DATA

p_{O_2}, mm	$Q+\Delta H_p+\varepsilon\beta$ (kcal/mole^{-1})	$\beta^\circ . K^\circ . k_p^\circ . p_{O_2}$	$K^\circ . k_p^\circ$, mm^{-1}	$Q+\Delta H_p$, kcal/mole^{-1}
20·0	20·9	$7{\cdot}6\times10^{-9}$	$3{\cdot}8\times10^{-10}$	19·4
1·2	22·0	$1{\cdot}4\times10^{-10}$	$1{\cdot}17\times10^{-10}$	20·5
0·4	21·5	$6{\cdot}3\times10^{-11}$	$1{\cdot}57\times10^{-10}$	20·0

oxygen the concentration of the radicals becomes less, which leads to a pronounced increase in the time of diffusion.

Results of calculations of the transformations according to the linear portions shown in Fig. 1 are summarized in the Table. In the calculation of the figures given in the 4th and 5th columns, we took into account the expression obtained in [1] for the thermal dependence of the coefficient β.

It can be seen from the table given that experiments carried out over a wide range of pressures of oxygen (from 20 to 0·4 mm) give approximately identical values for $K^{\circ} \cdot k_p$ and for $Q + \Delta H_p$. Thus:

$$Q + \Delta H_p = 20 \pm 0{\cdot}5 \text{ kcal/mole}^{-1} \quad (1)$$

$$K^{\circ} \cdot k_p^{\circ} \simeq 10^{-10} \text{ mm}^{-1}. \quad (2)$$

STUDY OF THE KINETICS OF THE DECOMPOSITION OF THE PEROXIDE RADICAL

With the object of studying the kinetics of the decomposition of the peroxide radical, we measured the concentrations of the radicals $\dot{R}O_2$ and $\dot{R}$, during the course of the continuous removal of oxygen at various temperatures, by the method of electron paramagnetic resonance. The kinetic curves proved to be essentially different for a sample consisting of leaves of thickness 0·25 mm and for a cylindrical sample with a diameter of 3·5 mm.

The kinetic curves for the thin leaves (Fig. 2, *a*) suggest, by their form, an ordinary monomolecular decomposition, while the kinetic curves for the cylindrical sample (Fig. 2, *b*) possess delayed initial portions, that is, the decomposition proceeds as if with an "induction period", decreasing with a rise of temperature. For comparison, on the right in the same Figure 2, *b* the kinetic diffusion curve (for $T = 163^{\circ}$) is given. From a comparison of the curves given, it follows that the initial portion in the decomposition curve is determined by the fact that, on pumping off, some time, approximately equal to the time of diffusion, is necessary for the escape of O_2 from the bulk of the sample. With a rise in the temperature, the time of diffusion and, consequently, the "induction period" naturally diminish. In the case of thin leaves, the time of diffusion is reduced, for example, 100-fold and, therefore, an initial portion similar to that shown in Fig. 2, *b* is not observed.

Figures 3, *a* and *b*, gives logarithmic transformations of the kinetic curves for the cylindrical sample and for the thin leaves. The deviation from rectilinearity in the case of cylindrical samples is explained by the reasons discussed above. In the calculations, these portions are, of course, not taken into account.

The existence of two rectilinear portions, with different slopes, in the case of the thin leaves may be explained if account is taken of the fact that, side by side with the removal of oxygen from the bulk of the material, the reverse of the decomposition reaction may proceed, with the addition of oxygen to the radical $\dot{R}$.

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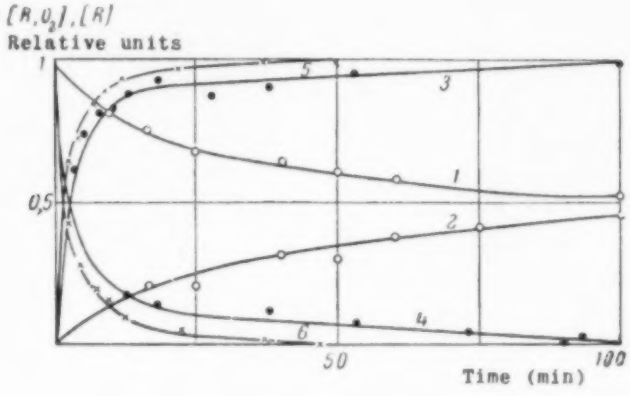
We shall write the processes taking place on pumping-off: $\dot{R}O_2 \xrightarrow{k_1} \dot{R} + O_2$, $\dot{R} + O_2 \xrightarrow{k_2} \dot{R}O_2$, $O_2 \xrightarrow{k_{diff}}$ removal*.



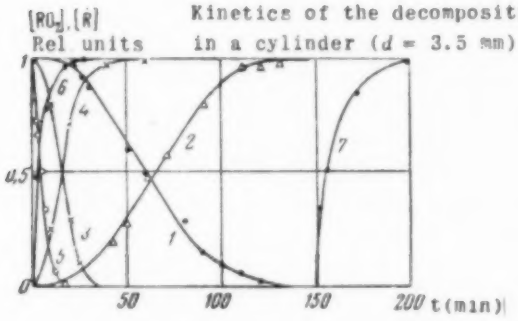


FIG. 2. Kinetics of the decomposition of $\dot{R}O_2$: *a* – in leaves with $\delta \simeq 0{\cdot}25$ mm; *b* – in a cylinder with $d = 3{\cdot}5$ mm:

a: 1 and 2 – 120°; 3 and 4 – 162°; 5 and 6 – 185°; *b*: 1 – 163°[$\dot{R}O_2$]; 2 – 163°[$\dot{R}$]; 3 – 198°[$\dot{R}O_2$]; 4 – 198°[$\dot{R}$]; 5 – 226°[$\dot{R}O_2$]; 6 – 226°[$\dot{R}$]; 7 – 163°[$\dot{R}O_2$].

Writing $[\dot{R}O_2] = n$, $[\dot{R}] = m$ and $O_2 = c$, we shall obtain the system of kinetic equations:

*The diffusion constant k_{diff} is connected with the diffusion coefficient by the well-known relation:

$$k = \pi \frac{D}{d^2},$$

where, for a cylinder, $\pi \simeq 32$ and d is the diameter, and for leaves $\pi \simeq 9{\cdot}9$ and d is the thickness.

Using the value of D obtained earlier [1], we have: for a cylinder $k_{diff} \simeq 5 \cdot 10^{-2} \cdot e^{-\frac{4600}{RT}}$ sec^{-1}, and for leaves

$$k_{diff} \simeq 3 \cdot e^{-\frac{4600}{RT}} \text{ sec}^{-1}.$$

$$\begin{cases} \dfrac{dc}{dt} = k_1 n - k_2 mc - k_{diff}\, c \\ \dfrac{dn}{dt} = -k_1 n + k_2 mc \\ m + n = n_0 \end{cases}$$

in which at $t = 0$, $n = n_0$ and $m = 0$.

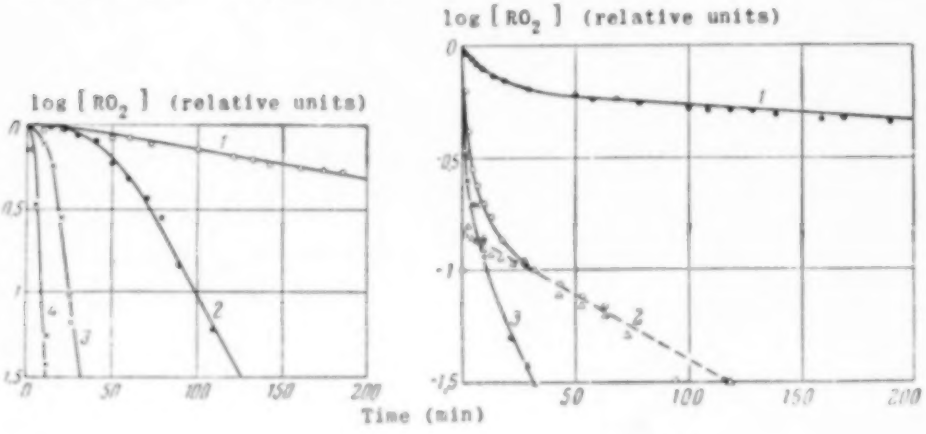


FIG. 3. Logarithmic transformations of the kinetics of the decomposition of RO_2: *a*—in a cylinder; *b*—in thin leaves:
a: 1—95; 2—163; 3—190°; 4—226°. *b*: 1—120; 2—162; 3—185°.

Since, in our case, O_2 is an intermediate product, we may, in accordance with Semenov's method of semi-stationary concentrations [2], assume, approximately:

$$\frac{dc}{dt} = 0 ,$$

then

$$c = \frac{k_1 n}{k_{diff} + k_2 m}$$

and

$$\frac{dn}{dt} = k_1 n \frac{k_{diff}}{k_2 m + k_{diff}} .$$

In the initial period, $m \ll n_0$ and $k_2 m \ll k_{diff}$ whence it follows that

$$\frac{dn}{dt} = -k_1 n .$$

That is, the initial portion of the kinetic curve corresponds to a true monomolecular decomposition and the tangent of the angle of slope of the linear portion in Fig. 3, *b* corresponds to the magnitude of the velocity constant of the decomposition k_1.

At higher degrees of conversion:

$$k_2 m \simeq k_2 n \gg k_{\text{diff}}{}^{*}$$

$$\frac{dn}{dt} \simeq -\frac{k_1 k_{\text{diff}}}{k_2 n_0} n$$

that is, the second rectilinear portion in Fig. 3, *b*, as also the rectilinear portion in Fig. 3, *a*, corresponds to a quasi-monomolecular law with an effective velocity constant:

$$k_{\delta\Phi\Phi} = \frac{k_1 k}{k_2 n_0} .$$

In order to describe the kinetics in the intermediate region of the change of n for the case of thin leaves (Fig. 3, *b*), it is necessary to integrate the expression:

$$\frac{dn}{dt} = -k_1 n \frac{k_{\text{diff}}}{k_2 (n_0 - n) + k_{\text{diff}}}$$

Assuming that the inequality $k_2 m \gg k_{\text{diff}}$ still holds, we obtain as a result:

$$l_n \frac{n_0}{n} = A - k_{\delta\Phi\Phi} t .$$

In Fig. 3, *b*, the dotted line shows the curve is rectified in the intermediate region if the values of $\log n - n_0/2{\cdot}3n$ are set off along the ordinate axis instead of $\log n$. The section of this equation close to $t=0$ is not given since, in this case, $k_2 m \ll k_{\text{diff}}$.

Fig. 4 gives the dependence on the temperature of the values of $\log k_1$ and $\log k_{\delta\Phi\Phi}$. From the dependence of $\log k_1$ on the reciprocal of the temperature, ε_1 and k_1—that is, the energy of activation and the pre-exponential factor of the velocity constant of the decomposition reaction—are readily determined. It should be noted that we always set the strength of the signal to the same initial figure; hence, no conversion factor enters into the calculation.

On the other hand, taking into account the fact that

$$\frac{k_2}{k_1} = K = K^{\circ} \cdot = e^{\frac{Q}{RT}} \quad \text{and} \quad k_{\text{diff}} = k^{\circ}_{\text{diff}} \cdot e^{-\frac{\varepsilon_{\text{diff}}}{RT}}$$

we obtain

$$\log k_{\delta\Phi\Phi} = \log \left(\frac{k^{\circ}_{\text{diff}}}{K^{\circ} \cdot n_0} \right) - \frac{Q + \varepsilon_{\text{diff}}}{2{\cdot}3\, RT} .$$

* The applicability of this inequality follows from the following quantitative considerations. It will be shown below that $k_2 \approx 10^{-15} \cdot e^{-\frac{6000}{RT}}$ cm³/sec; taking into account that $n_0 \simeq 10^{18}$ cm^{-3}, and $k_{\text{diff}} \simeq 3 \cdot e^{-4600/RT}$ sec^{-1} for leaves [1], we shall have:

$$\frac{k_2 m}{k_{\text{diff}}} = \frac{10^{-15} \cdot e^{-\frac{6000}{RT}} \cdot 10^{18}}{3 \cdot e^{-\frac{4600}{RT}}} \approx 3 \cdot 10^{2} \cdot e^{-\frac{1400}{RT}} = 10^{2{\cdot}5 - \frac{300}{T}} \gg 1 \text{ if } T > 300^{\circ} K .$$

From Fig. 4 it can be seen that the value of $(k^{\circ}_{diff}/K^{\circ}\cdot n)$ for the thin leaves differs from the value of this magnitude for the cylinder by a factor of about 10. However, the value of k°_{diff} as we showed earlier, differs by a factor of about 100. The total concentrations of radicals in our samples was about 10^{17}–10^{18} cm^{-3}.

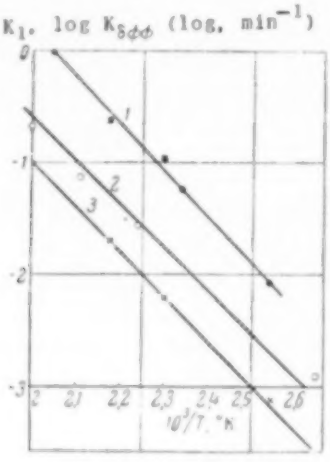


FIG. 4. Temperature dependence of the velocity constant for the decomposition of $\dot{R}O_2$

1 – $\log k_1 = (9 \pm 1) - (20 \pm 1)10^3/RT$; 2 – $\log k_{3\phi\phi} = (7 \pm 1) - (18 \pm 1)10^3/RT$ (cylinder); 3 – $\log k_{3\phi\phi} = (6 \pm 1) - (19 \pm 1)10^3/RT$ (leaves).

this figure being somewhat higher in the case of the leaves. Hence, it follows that a 10-fold change in the magnitude $k^{\circ}_{diff}/K^{\circ}$ is consistent with the calculated value within the limits of error.

We may, consequently, determine the values of K° and $Q+\varepsilon_{diff}$ from the data of Fig. 4. We shall take the calculated values of these magnitudes determined from the kinetics of the decomposition of $\dot{R}O_2$:

$$\varepsilon_1 = Q - \varepsilon_2 = 20 \pm 1 \text{ kcal/mole}, \tag{3}$$

$$Q + \varepsilon_{diff} = 18{\cdot}5 \pm 2 \text{ kcal/mole}, \tag{4}$$

$$k^{\circ}_1 = 8 \pm 1, \tag{5}$$

$$K^{\circ} = -23 \pm 1. \tag{6}$$

We know [1] that $\varepsilon_{diff} = 4{\cdot}6 \pm 0{\cdot}5$ kcal/mole, therefore, combining (1), (3) and (4), we obtain

$$Q = 14 \pm 2{\cdot}5 \text{ kcal/mole},$$

$$\varepsilon_{diff} = 6 \pm 3{\cdot}5 \text{ kcal/mole, and}$$

$$\Delta H_p = 6 \pm 2{\cdot}5 \text{ kcal/mole},$$

and, combining (2) and (6), we obtain:

$$k_2^0 \simeq 10^{-15}\ \text{cm}^3/\text{sec}, \text{ and}$$

$$k_p^0 \simeq 10^{13}\ \text{cm}^{-3}/\text{mm}.$$

Finally, the results of the measurements may be written in the form:

$$k_1 \simeq 10^8 . e^{-\frac{20000}{RT}}\ \text{sec}^{-1} = 10^{-5}\, \nu_0 . e^{-\frac{20000}{RT}}\ \text{sec}^{-1};$$

$$k_2 \simeq 10^{-15} . e^{-\frac{6000}{RT}}\ \text{cm}^3/\text{sec} = 10^{-5}\, z^0 e^{-\frac{6000}{RT}}\ \text{cm}^3/\text{sec};$$

$$K \simeq 10^{-22} e^{\frac{14000}{RT}}\ \text{cm}^{-3};$$

$$k_p \simeq 10^{13} e^{\frac{6000}{RT}}\ \text{cm}^{-3}/\text{mm} \simeq 10^{-2}\, e^{\frac{6000}{RT}}\ \frac{\text{cm}^3 \text{ of dissolved oxygen}}{\text{cm}^3 \text{ of sample. mm}}\ *$$

In our considerations we have always assumed that the time for the addition of the oxygen was less than the time of diffusion. We shall check the accuracy of this assumption. Using the data given in [1], we obtain for the time of diffusion in the case of leaves:

$$\tau_{\text{diff}} \sim \frac{1}{k_{\text{diff}}} \sim \frac{1}{3 . e^{-\frac{4600}{RT}}} \sim 10^{\frac{1000}{T} - 0.5}\ \text{sec},$$

and the time for the reaction, from our own data:

$$\tau_2 \sim \frac{1}{k_2 \nu_0} \sim \frac{1}{10^{-15} . e^{-\frac{6000}{RT}} . 10^{18}} \sim 10^{\frac{1300}{T} - 3}\ \text{sec},$$

that is, at room temperature $\tau_{\text{diff}} \sim 10^2$ sec and $\tau_2 \sim 20$ sec. For cylindrical samples, τ_{diff} is 100 times greater.

DISCUSSION OF THE RESULTS

The absence of information on the constants of radical reactions in the solid phase makes it impossible to compare our results with the data of other authors. However, on comparison with reactions of similar type in a gaseous or liquid phase the magnitudes of the heat effect of the reaction (14 kcal/mole) and of the energy of activation (6 and 20 kcal/mole) appear completely reasonable. In particular, the values $Q = 14$ kcal/mole and $\varepsilon_2 = 6$ kcal/mole agree very well with the empirical relation between the energy of activation and the heat effect

* Nikolayeva in our laboratory has carried out the direct measurement of the solubility constant of oxygen in irradiated teflon at room temperature. The value of k_p obtained by her agrees with ours within the limits of accuracy.

of the reaction of the addition of radicals $\varepsilon = A - \alpha Q$ [3]. These values of ε_2 and Q are also close to the corresponding magnitudes for reactions of the type $\dot{R} + {+}R'C{=}C-$ and $\dot{C}H_3 + RC{=}O$.

The value of the steric factor (10^{-5}) for the addition $\dot{R} + O_2$ may also be compared with the value of the steric factor for the addition of oxygen to tetrafluoroethylene, which has been shown to be $3 \cdot 10^{-5}$ [4]. The very small value (10^{-5}) of the steric factor for the decomposition of the peroxide radical is more unusual. Probably the crystalline structure creates an additional geometrical hindrance, in comparison with a gaseous medium, to the breaking away of the oxygen molecule.

The value of the pre-exponential factor of the solubility constant obtained by us (10^{-3} cm³ of dissolved gas per 1 cm³ of sample per mm) agrees well with the figures given in the literature [5] for other polymers. The heat of solution has, however, proved to be 3–4 times greater in our case.

The authors express their thanks to B. T. Nakrokhina for presenting the thin teflon leaves on which the experiments described were carried out.

CONCLUSIONS

1. With the aid of the method of electron paramagnetic resonance, the equilibrium between the radicals $\dot{R}$ and $\dot{R}O_2$ in irradiated teflon and the kinetics of the decomposition of the radical $\dot{R}O_2$ at various temperatures have been studied.

2. The features of the kinetic curves have been explained as functions of the dimensions of the sample and the degree of conversion.

3. On the basis of an analysis of the experimental results, the following have been calculated:

a) the equilibrium constant for:

$$\dot{R}O_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} \dot{R} + O_2 ,$$

$$K \simeq 10^{-22} \cdot e^{\frac{14000}{RT}} \text{ cm}^{-3};$$

b) the velocity constants for the direct and reverse reactions:

$$k_1 \simeq 10^{9}\, e^{-\frac{20000}{RT}} \text{ sec}^{-1},$$

$$k_2 \simeq 10^{-15}\, e^{\frac{6000}{RT}} \text{ cm}^3/\text{sec}; \text{ and}$$

c) the solubility constant for oxygen:

$$k_p \simeq 10^{-3}\, e^{\frac{6000}{RT}} \frac{\text{cm}^3 \text{ dissolved oxygen}}{\text{cm}^3 \text{ sample} \cdot \text{mm}}.$$

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POLYMERS WITH CONJUGATED BONDS* IN THE MACROMOLECULAR CHAINS—IV. ON SOME CHARACTERISTICS OF POLYMERIC COMPOUNDS CONTAINING HETEROATOMS IN THE CONJUGATED CHAIN†

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IN a previous communication [1] it was shown that carbon-chain polymers with a system of conjugated bonds in the macromolecule are characterized by the presence of a fairly large quantity of unpaired electrons in the ground state of the system, these electrons being delocalized with respect to the system of conjugated bonds and belonging to the molecule as a whole. The polymers referred to contained only carbon and hydrogen and therefore did not contain in their composition any polar groups and electron-donor or electron-acceptor centres. In the present work we have attempted to investigate the influence of heteroatoms (nitrogen and oxygen), and also of metal atoms, on the magnetic properties of polymers with conjugated bonds under the condition that these atoms are present in the basic conjugated chain. As will be seen below, it has been, surprisingly, possible to obtain completely new effects. In order to investigate this question, two of us carried out the synthesis of macromolecules containing continuously alternating polar groupings and heteroatoms in the conjugated chain [2]. Among these polymers are the poly(aminoquinones) formed in the reaction of benzidine with chloroanil in the presence of sodium acetate in an ethyl alcohol or dimethylformamide medium.

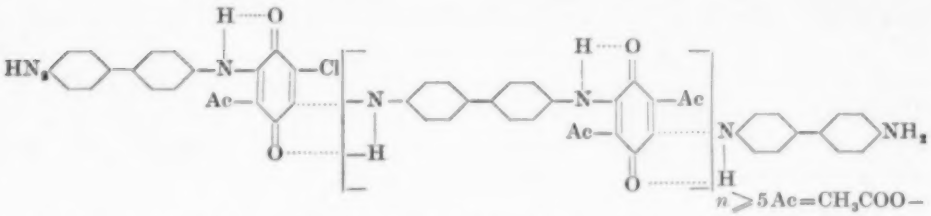
Dark brown inflexible polymers which are soluble in mineral acids and formic acid and partially soluble in dimethylformamide are formed as a result of the reaction.

Investigation of the infra-red spectra showed the presence of imino groups and hydrogen bonds.

The results of micro-analysis in combination with the study of the infra-red spectra, taking account of the mechanism of the reaction of chloranil with aromatic amines [3], makes it possible to put forward the following structure for the polymer synthesized:

* *Sic*, here and elsewhere. Strictly, it should be "conjugated double bonds" (Translator)

† Vysokomol. soedin. **1**: No. 11, 1647–1651, 1959.



It can be seen from the formula adduced that conjugation extends along the whole chain of the macromolecule, coming into being, obviously, at the expense of the aromatic form of the quinone rings. In the given case, it is possible to assume the presence of not only intramolecular but also intermolecular hydrogen bonds, which may lead to a three-dimensional formation and to diminished solubility.

In order to elucidate the rôle of conjugation in the emergence of anomalous magnetic properties, poly(aminoquinones) were obtained from chloranil and hexamethylenediamine. The electron paramagnetic resonance (EPR) spectra were recorded on the spectrometer described in a previous communication [4].

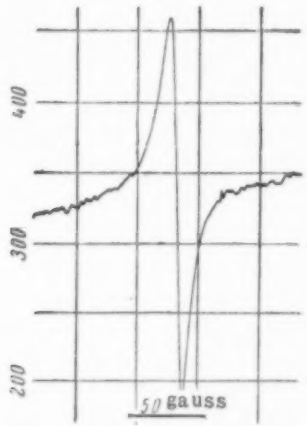


FIG. 1. Sharp EPR sigutl of poly(aminoquinone)

The poly(aminoquinones) synthesized from chloranil and hexamethylenediamine do not exhibit EPR absorption. Thus, for magnetic effects to be observed, conjugation is necessary. It must be noted that the starting materials for the synthesis of the poly(aminoquinones) also do not exhibit EPR absorption.

The aromatic poly(aminoquinones) are characterized by EPR spectra the intensity of which grows with the degree of polymerization. As in the case of carbon-chain polymers with a system of conjugated bonds in the main chain considered earlier [1], the poly(aminoquinones) exhibit a sharp EPR signal with the distance between the points of maximum slope 8 oersteds and with the g-factor of the

free electron devoid of fine structure, indicating the presence in the ground state of the system of unpaired electrons delocalized with respect to the system of conjugated bonds (Fig. 1). The concentration of unpaired electrons depends on the degree of polymerization and amounts to 10^{17}–10^{18} per g. In addition to these lines, at a sufficient degree of polymerization broad asymmetrical EPR lines wth a considerably greater total intensity are observed.

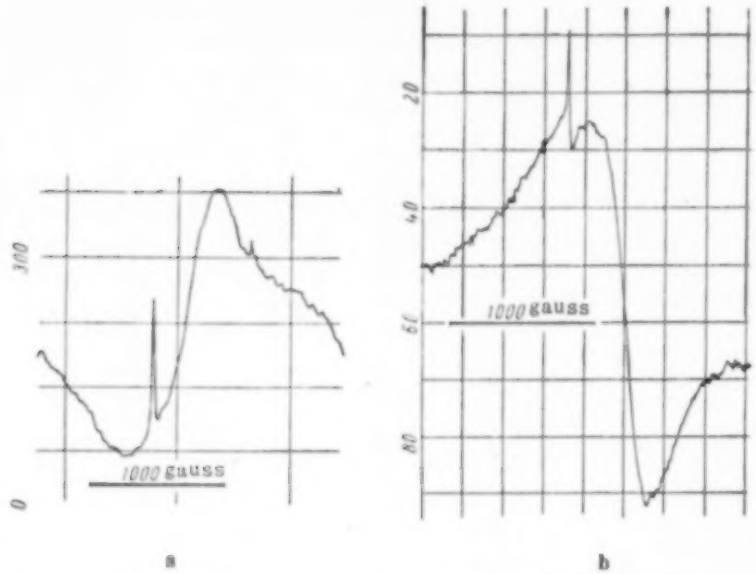


FIG. 2. EPR spectrum: *a* – a soluble poly(aminoquinone) obtained from chloranil and benzidine in dimethylformamide in the presence of an excess of sodium acetate (polymer 1); *b* – an insoluble poly(aminoquinone) obtained under the same conditions (polymer 2).

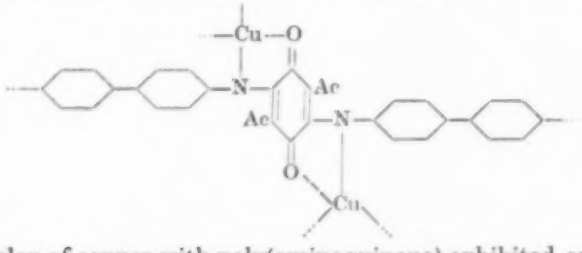
In Fig. 2, a and b, are given the EPR spectra for poly(aminoquinones) of different degrees of polymerization, taken over a wide range of magnetic fields. The concentration of unsaturated electrons amounts 10^{20}–10^{21} per g. The g-factors are shifted from the g-factor of the free electron in the direction of higher values by some units in the first place after the comma [i. e., decimal point]. The asymmetry of the lines indicates the great g-factor anisotropy and, consequently, the presence in the system of intrinsic internal anisotropic fields. The breadth of the lines between the points of maximum slope is 500–600 oersted and the wings of the lines extend many thousand oersted. On reducing the temperature to 80° K, the EPR absorption disappears with a suddenness that suggests the behaviour of paramagnetic substances with antiferromagnetic properties. Thus, it is possible to state that, in the polymeric systems considered, with polar groups and heteroatoms in the chain of conjugation, an enormous cloud of strongly interacting

unpaired electrons arises in the ground state, creating anisotropic internal magnetic fields in the molecule. For such systems it is possible to anticipate dependencies of the magnetic susceptibility on the intensity of the internal magnetic field characteristic for ferromagnetic and antiferromagnetic substances. The sudden disappearance of EPR absorption at low temperatures may be explained, as in the case of antiferromagnetic substances, by an ordering of the structure, which leads to the appearance of such strong anisotropic internal fields that the Zeeman levels are split in the zero internal magnetic field by an amount greater than the energy of the high-frequency quanta. It must be noted that the upaired electrons giving a broad EPR signal have a completely different nature from the delocalized electrons giving sharp EPR signals, since the dependence of the signals on the temperature is completely different. Up to the present, similar effects have been observed only in compounds of the type of Cr_2O_3, CuO, MnSe and the like, containing atoms of metals with unpaired *d*-electrons in the atom electron shells.

It is interesting that analogous effects have been observed by two of us [4] with nucleic acids and their complexes with proteins. It may be said that the polymers considered in the present work are, in a well-known sense, chemical molecules by the study of which one may hope to understand the nature of the anomalous magnetic properties of these very important biopolymers. One must beware of too far-reaching analogies since there is no conjugation in the nucleic acids extending along the chain of the macromolecule, which is shown by the fact that they are colourless. Hence, the origin of the unpaired electrons in the case of the nucleic acids may be completely different. It is possible, however, that the origin of the unpaired electrons giving the broad EPR lines is connected in both cases not with the presence of a system of conjugated bonds but with an ordered system of polar groups.

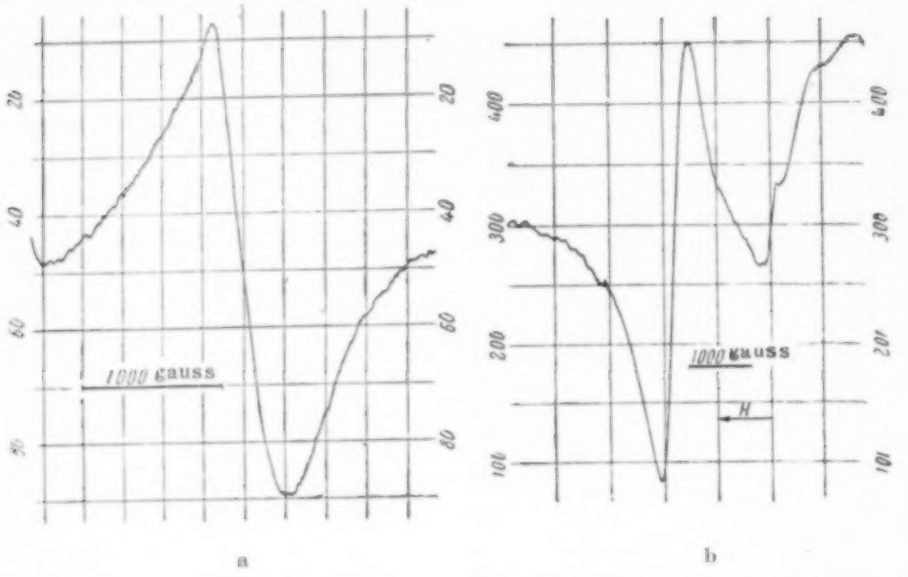
We also carried out an investigation of the EPR spectra of complexes of poly-(aminoquinones) with copper. The complexes were obtained by the reaction of a solution or suspension of the polymer with copper acetate; the content of copper in the complex was 8–15%.

It may be assumed that the copper ions additionally increase the structural complexity of the system and form a three-dimensional network of the following formula:



The complex of copper with poly(aminoquinone) exhibited an EPR spectrum (see Fig. 2, *b*) practically identical with the spectrum of the same polymer with

a higher degree of polymerization (polymer 2) that is, the introduction of the copper only increased the intensity of the signal (Fig. 3, *a*). The EPR spectrum of the copper complex with poly(aminoquinone) also gives a broad asymmetrical EPR line, which differs from the spectrum of the initial polymer by the strong absorption at zero field (Fig. 3, *b*).



a b

FIG. 3. EPR spectrum: *a*—complex of polymer 1 with Cu^{+2}; *b*—complex of polymer 2 with Cu^{+2}.

It is interesting to note that, in distinction from the EPR spectra of the initial polymers, the spectra of the complexes do not disappear at the temperature of liquid nitrogen. It is possible that the transition point lies even lower in this case. On the basis of the data given, it is possible to assume that the influence of complex formation with metals on the EPR spectrum of the polymers considered is connected with the additional structural complexity and not with the presence along with the metal ions of their own unpaired d-electrons.

The results presented in the present communications give grounds for assuming that further investigations in the field of polymers containing heteroatoms and polymer groupings in a conjugated chain, and also their complexes with metallic ions, may lead to the creation of new classes of polymeric substances.

CONCLUSIONS

(1) The EPR spectra of polymers of the series of poly(aminoquinones) and their complexes with copper have been studied.

(2) The polymers give intense broad asymmetrical EPR lines, indicating the presence of a large quantity (10^{20}–10^{21} per g) of strongly interacting unpaired

electrons. These lines and their changes with temperature are extremely reminiscent of the EPR spectra of paramagnetic substances of the type of Cr_2O_3 possessing antiferromagnetic properties.

(3) In addition to the broad line, sharp lines are observed in the EPR spectrum with the g-factor of a free electron; these arise in all polymers with conjugated bonds in the main chain. At reduced temperatures the intensity increases, as for ordinary paramagnetic substances.

(4) The introduction of a metal into the polymer does not lead to any specific change in the magnetic properties of the polymer. The change in EPR spectrum observed on complex formation may be explained by the additional structural complexity caused through the co-ordination bonds of the metal atoms.

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EXCLUDED VOLUME IN THE THEORY OF SWOLLEN NETWORK POLYMER DEFORMATION*

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INTRODUCTION

THE present statistical theory of network polymer (rubber) deformations [1, 2] does not take into account intermolecular interaction and is only in rough qualitative agreement with experimental data. To assess intermolecular interaction is difficult—we are ignorant even of the nature of those interaction forces responsible for the divergence between theory and experiment.

We shall consider the simplest interaction—that linked with the fact that a volume occupied by some molecule or other is inaccessible to the others. The excluded volume effect is in many cases examined in the light of the polymer solutions theory [2], where the so-called "pearl necklace" model is used, in which it is supposed that the polymer molecule consists of freely-coupled segments which interact among themselves by central forces. In assessing volume effects in the high-elasticity theory, it is natural to take the "pearl necklace" network as a model.

Taking a heavily swollen polymer, in which the excluded volume is much less than the full volume of the test piece, small-parameter expansion may be used.

Arguments are given in a paper [3], based on a "pearl necklace" model, demonstrating that volume effects play a major role in the network polymer deformation theory. We give here the further development of the application of the "pearl necklace" to the network of a swollen polymer.

FREE NETWORK ENERGY WITH LOW CENTRAL INTERACTION FORCES

Many works on polymer solution theory in which the necklace model has been used have borrowed small-parameter expansion from the real gas theory. This method was used in [3] to obtain an expression for free network energy in a linear approximation. With quadratic term accuracy, this expression takes the form

$$\psi = \psi_0 - kT[\beta Q_z + \beta^2 (Q_{zz} - Q_z^2)/2]. \tag{1}$$

* Vysokomol. soedin. **1**: No. 11, 1659–1669, 1960.

Here the first irreducible integral is $\beta=\int[\exp(-u/kT)-1]d\vec{r}$, where u is the energy of paired segment interaction and r is the vector, writing them:

$$Q_2=\frac{1}{2}\sum_{i\neq k}P(i;k), \quad Q_{22}=\frac{1}{4}\sum_{i\neq k\neq m\neq n}P[(i,k)(m,n)]$$

where $P(i,k)$ is the density of probability of "collision" between segments i and k, i.e., of the fluctuation resulting in the distance between segments i and k becoming equal to zero, and $P[(i,k)(m,n)]$ is the probability density of a "collision" of the i-th segment with the k-th and the m-th with the n-th simultaneously, these probabilities being calculated in a network without interaction (when $u=0$). ψ_0 is the free energy of such a network, and kT the statistical temperature.

Expansion (1) was obtained by formal use of real gas theory methods. To give it some foundation, the magnitude of the dimensionless parameter of expansion (1) must be assessed. In the proposition that a network without interaction is Gaussian, an estimation of Q_2 was produced in [3]. We shall here make a similar estimation of the following term.

Let us introduce the designations $\vec{r}_i$—radius vector of the i-th segment: $\vec{r}_{ik}=\vec{r}_i-\vec{r}_k$—the vector uniting segments i and k; $\vec{r}_{0,ik}$—mean value of $\vec{r}_{ik}$; $\vec{R}_{ik}=\vec{r}_{ik}-\vec{r}_{0,ik}$—deviation from mean value.

James [4] developed the theory of fluctuations in a Gaussian network of non-interacting chains, in which the distribution for vectors $\vec{R}_{ik}$ and $\vec{R}_{mn}$ has the form

$$\rho(\vec{R}_{ik},\vec{R}_{mn})=\rho(\vec{R}_i k)\,\rho(\vec{R}_{mn})\,(1-\delta^2_{ikmn})^{-3/2}\times\exp\left[-\frac{3}{2a^2(1-\delta^2)}\left(\frac{\delta^2R^2_{ik}}{Z_{ik}}+\right.\right.$$
$$\left.\left.+\frac{\delta^2R^2_{mn}}{Z_{mn}}-\frac{2\delta\,\vec{R}_{ik}\vec{R}_{mn}}{\sqrt{Z_{ik}Z_{mn}}}\right)\right]. \qquad (2)$$

Here the distribution for vector R_{ik} has the form

$$\rho(\vec{R}_{ik})=\left(\frac{3}{2\pi Z_{ik}a^2}\right)^{3/2}\exp\left(-\frac{3R^2_{ik}}{2Z_{ik}a^2}\right) \qquad (3)$$

and $\rho(\vec{R}_{mn})$ is written in a like fashion; a is the length of the segment, Z_{ik} the distribution parameter with the sense of the effective number of segments, and δ_{ikmn} the correlation coefficient. Z_{ik} and δ_{ikmn} are determined by the network structure. We shall obtain the values of $P(i,k)$ and $P[(i,k)(m,n)]$ after putting in (2) and (3).

$$\vec{R}_{ik}=-\vec{r}_{0,ik}, \quad R_{mn}=-\vec{r}_{0,mn}.$$

Using the distribution functions properly obtained $Q_{22}-Q_2^2$ may be written in the form of an integral

$$Q_{22}-Q_2^2=N\int_V \vec{dr}_1\int_V \vec{dr}_2\int_V \vec{d\rho}\int dZ_1\int dZ_2\int d\delta N(\rho)\times$$

$$\times W_4(\delta;\vec{r}_1,\vec{r}_2,\vec{\rho})\,K(\vec{r}_1^*,\vec{r}_2^*,Z_1,Z_2,\delta)\times \tag{4}$$

$$\times\prod_{s=1}^{2} N(r_s)\,W_2(Z_s,\vec{r}_s)\,P(\vec{r}_s^*,Z_s).$$

Here N is the complete number of segments in the network, V is the test-piece volume, $N(r)dr$ is the number of pairs of segments divided by N, the distance between which lies in the circumference of dr near the value of r,* $W_2(Z, r)dZ$ is the probability of encountering a pair of segments divided by distance r, in which the distribution parameter (3) lies on the circumference of dZ near the value of Z, $W_4(\delta; r_1, r_2, \rho)$ is the probability of encountering a quartet of segments, in which the 1st and 2nd are linked by vector $\vec{r}_1$, the 3rd and 4th by vector $\vec{r}_2$, the 1st and 3rd by vector $\vec{\rho}$, and the coefficient of correlation lies on the circumference of $d\delta$ near value δ. On the basis of the properties of a Gaussian network [4], $\vec{r}_s^*$ is a vector with components $\lambda_1 x_s$, $\lambda_2 y_s$, $\lambda_3 z_s$ where x_s, y_s, z_s are components of vector $\vec{r}_s$ and λ_1, λ_2, λ_3 are the main expansion factors; the form of functions

$$P(\vec{r}_s^*, Z_s) \text{ and } K(\vec{r}_1^*, \vec{r}_2^*, Z_1, Z_2, \delta)$$

is clear from (2) and (3). We shall go over in (4) to dimensionless variables:

$$\sqrt{3/2\,na^2}r_s=u_s,$$

where n is the mean number of segments in a chain (a chain signifies a section of a polymer molecule between two adjacent network points);

$$\chi=\rho/h$$

where h is the distance between the chain ends, averaged for fluctuations and grid; $v_s=Z_s/n$ where v is the volume fitting one segment. Given uniform distribution of the segments in space, $f(u)=1$, and it follows that in a real network $f(u)$ is close to unity everywhere, excluding, perhaps, small regions. Integral (4) thus assumes the form

$$Q_{22}-Q_2^2=\frac{Nh^2}{4\pi^2v^2}I_2. \tag{5}$$

Here

$$I_2=\int du_1\int du_2\int dv_1\int dv_2\int d\chi\int d\omega_\chi\int d\delta f(\chi)\,W_4(\delta;\vec{u}_1,\vec{u}_2,\chi)\times$$

* For the sake of brevity, when speaking here and later about segment positions, we shall assume this to mean the mean distances in the undeformed state.

$$\times K(\vec{u}_1^*, \vec{u}_2^*, v_1, v_2, \delta) \prod_{s=1}^{2} W_s(v_s, u_s) \exp(-u_s^{*2}/v_s), \tag{6}$$

where dw_χ is the angular part of $d\vec{\chi}$, $\vec{u}_s^*$ being obtained from $\vec{u}_s$ as $\vec{r}_s^*$ from $\vec{r}_s$.

A major problem now faces us: does the integral converge along χ when $v \to \infty$. If this integral diverges, it follows that the real gas theory methods are inapplicable to the grid.

We have sound enough arguments in favour of the convergence of integral (6) along χ.

Using James' [4] method of examining the correct cubic tetra-functional network, i.e., a network, all of whose chains consist of an identical number of segments n, and the points form a cubic lattice, there being 6 chains issuing from each point, we can find the coefficient of correlation for the points of such a network. The points are determined by 3 numbers—r, s and t, such that rh, sh, and th are the coordinates of the given point (mean position in undeformed state). The crux of James' method lies in the introduction of normal coordinates:

$$\vec{R}_{r,s,t} = \sum_{a,b,c} \vec{q}_{a,b,c} \Phi(a, b, c; r, s, t), \tag{7}$$

where $\Phi(a, b, c,; r, s, t)$ is the function determined by James, and the area of change of magnitudes a, b and c is the same as for r, s, t. We are concerned here with the correlation coefficient between vector

$$\vec{R}_{r,s,t;\,u,v,w} = \sum_{a,b,c} \vec{q}_{a,b,c} [\Phi(a, b, c; r, s, t) - \Phi(a, b, c; u, v, w)] \tag{L}$$

and vector $\vec{R}_{r',s',t';\,u',v',w'}$ which is determined in a like manner. On the basis of the Win-Chen Wang-Uhlenbeck theory [5] on the multidimensional Gaussian function, we find that the desired correlation coefficient is determined by the formula

$$\delta_{1\cdot 2} = \frac{1}{\sqrt{Z_1 Z_2}} \sum_{a,b,c} [\Phi(a, b, c; r, s, t) - \Phi(a, b, c; u, v, w)] \times \\ \times [\Phi(a, b, c; r', s', t') - \Phi(a, b, c; u', v', w')], \tag{8}$$

where 1 signifies the set of indices r, s, t; u, v, w and 2—the set of indices r', s', t'; u', v', w'. We introduce the vectors: $-\vec{\chi}$ with components: $r-r'$; $s-s'$; $t-t'$; $\vec{u}_1$ with components $(r-u)/p$; $(s-v)/p$; $(t-w)/p$; and $\vec{u}_2$ with components $(r'-u')/p$; $(s'-v')/p$, $(t'-w')/p$, where $p=(3/2na^2)^{1/2}(h/a)$. (9)

Using James' calculations [4] of expressions like (8), we obtain

$$\delta_{1\cdot 2} = \frac{1}{4\pi\sqrt{v_1 v_2}} \left(\frac{1}{\vec{\chi}} - \frac{p}{|p\vec{\chi} + \vec{u}_1|} - \frac{p}{|p\vec{\chi} - \vec{u}_2|} + \frac{p}{|p\vec{\chi} + \vec{u}_1 - \vec{u}_2|} \right). \tag{10}$$

where v_1, v_2 were introduced previously (6). It follows from (10) that when $\chi \to \infty$ $\delta = O(\chi^{-3})$. For greater χ, the correlation coefficient may be considered

a function from $\vec{u}_1, \vec{u}_2, \vec{\chi}$. And, as $W_4(\delta; \vec{u}_1; \vec{u}_2; \chi)$ is the distribution averaged for the grid, we can hope that (10) is good for all segments of the grid, not just the points.

If we expand $K(\vec{u}_1, \vec{u}_2, v_1, v_2, \delta)$ into a series for δ, the zero term returns to zero. On integrating δ, which was determined by formula (10), for the angular variables dw_χ, the integral will equal zero. Hence the behaviour of K when $\chi \to \infty$ will be determined by the behaviour of the term with δ_2, i.e., the integral along χ converges, and rapidly at that. There is no cause to think that the conclusion obtained will not be true for any other three-dimensional network, in particular, the tetrafunctional network.

However, since what has been given above can in no way be considered a proof, we shall henceforth take the sufficient speed of convergence of the integral (6) along as an hypothesis.

The sub-integral expression in (6) contains no large or small parameters. We shall thus say in this context that I_2 has "the order of one". Kubo [7] obtained the relationship

$$h^2 = \tau n v ,$$

where τ is a numerical constant dependent on the network construction. (It can be demonstrated that for an isotropic, in the undeformed state, orderless network, $\tau = 8$). Using (11) we rewrite (5) in the form

$$Q_{11} - Q_1^2 = N v^{-2} \tau^3 n I_2 \tag{12}$$

The same estimation of Q_2 (cf. [4] gives

$$Q_2 = N v^{-1} I_1 , \tag{13}$$

where I_1 has "the order of one" in the same sense as has I_2. ψ_s may, from James [5], be written in the form

$$\psi_s = kTGI_0 , \tag{14}$$

where G is the number of chains in the network ($nG = N$) and I_0, like I_1 and I_2 is a dimensionless function of deformation variables "of the order of one".

Comparing (12), (13) and (14), we see that the expansion parameter in (1) is

$$x = n\beta v^{-1} . \tag{15}$$

If we use v_0 to designate the volume fitting one segment in the non-swollen state, then $v_0/v = v_r$—the degree of swelling, and the expansion parameter may be written in the form

$$x = n\beta v_r v_0^{-1} . \tag{16}$$

In the theory of volume effects in polymer solutions, the dimensionless parameter $\zeta = n^{1/2}\beta a^{-3}$ is often introduced. Using (11), x may be expressed in the form $x = \tau (3/2)^{3/2} \zeta p^{-3}$, where p was introduced previously (9).

It is important to find out whether it is possible to attain degrees of swelling at which x will be small, while the Gaussian approximation for a network without

interaction remains valid. Treloar [1] showed that the Gaussian approximation is valid until relative dilation of the chains exceeds 1/3 or even 1/2. Using (11), we write

$$v_r = \tau v_0 / n^2 a^3 t^3 .$$

It follows that at sufficiently large n, i.e., in low-vulcanized rubbers, x may be made small, but the Gaussian approximation remains valid.

However, such high degrees of swelling in fact exceed those obtained so far in experimental work. Expansion (1) may, however, be advantageous not only at small values of the parameter x, for the idea of "the order of one" does not have its usual sense in this sector. It may be found that coefficients I_1 and I_2, or their deformation variable derivatives will be so small, that (1) will also hold for the x values met with in experiments. This problem can be solved only by concrete calculations and comparison with experiments.

To enable a shift to concrete calculations, the distribution of relative fluctuations must be found.

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DETERMINING THE PARAMETER OF RELATIVE FLUCTUATIONS IN A GAUSSIAN NETWORK OF CHAINS WITH AN IDENTICAL NUMBER OF SEGMENTS

In [7] we were given an approximated method of estimating fluctuation distribution parameters in a Gaussian network, in which a small part (cell) of the network—so small that the ratios of James' general theory [5] could be used easily—was examined instead of the entire network, assuming that all the chains consist of an identical number of segments n, and that all points are completely identical. The functionality of the network q, i.e., the number of chains coming from one point, may be any.

In the first approximation we take as the "cell" the chains coming from one point, and assume that the fluctuations of the ends of these chains are independent. In this approximation in [7] the distribution of chain and fluctuations in relative to the beginning was found. It is likewise possible to find that the parameter Z_{ik}, where i and k are the number of segments of one chain, reckoned off from its beginning, is determined by the relationship

$$Z_{ik} = |k-i|[1-|k-i|(q-2)/qn] . \tag{17}$$

If, however, segments i and k belong to neighbouring (coming from one point) chains and i and k are the number of segments reckoned off from a common point, parameter Z_{ik} has the form

$$Z_{ik} = i+k-\frac{q-2}{q(q-1)n}[(q-1)(i^2+k^2)+2ik] . \tag{18}$$

It is interesting to compare (18) with James' formulae [4] for a correct cubic hexafunctional network. When $q=6$, $i=n$ and $k=n$ (18) gives $Z_{nn}=0{\cdot}4n$, and by James' formula $0{\cdot}42n$ or $0{\cdot}39n$, depending on the angle between the chains. The agreement is within the limits of accuracy of James' formula.

To construct a second approximation cell, we shall join to the ends of the chains of the first approximation cell, which we shall from now on term the first points, all the remaining chains coming from these points. A diagram of a second approximation cell is to be seen in Fig. 1. The first points we shall designate by indices from 1 to q. The second points, i.e., the chain ends, coming from the first points, will be designated by two indices; the first index indicates the first point, to which the given second belongs, and the second index (*after the occupied one**) is the number of the given point in the group of second points to which it belongs.

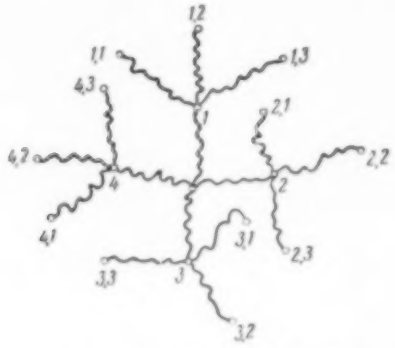

FIG. 1. Scheme of second approximation cell for a tetrafunctional network.

Second indices change from 1 to $q-1$. Thus $r_{i,k}$ designates the radius-vector of a second point with indices i and k. The second approximation consists in the hypothesis that the fluctuations of second points belonging to different first points are independent, i.e., the distribution of second point fluctuations has the form:

$$\rho(\vec{R}_{1,1}\dots\vec{R}_{q,q-1})\sim\prod_{i=1}^{q}\exp\left[-\frac{3}{2n\sigma^2}\left(\mu\sum_{k=1}^{q}R_{i,k}^2-\nu\sum_{k\neq l}\vec{R}_{i,k}\vec{R}_{i,l}\right)\right], \tag{19}$$

where, as before $\vec{R}_{i,k}=\vec{r}_{i,k}-\vec{r}_{0,i,k}$. The fact that the coefficients coming before the squares of the displacement vectors, are to equal all μ, and the paired products in front of them all equal ν, is a consequence of the hypothesis on the equitability of all the points. Distribution of the fluctuations for the central point may be written in the form:

$$\rho(\vec{R})=\int\rho(\vec{R}/\vec{R}_{1,1}\dots\vec{R}_{q,q-1})\,\rho(\vec{R}_{1,1}\dots\vec{R}_{q,q-1})\,dR_{1,1}\dots dR_{q,q-1}, \tag{20}$$

where the conditional distribution for the central point for the given positions of the second points $\rho(\vec{R}/\vec{R}_{1,1}\dots\vec{R}_{q,q-1})$ is found on the basis of James' general theory. On the other hand, integrating (19) for all $\vec{R}_{i,k}$ except one, we obtain the distribution for the second point. The equality of distributions for the central

* Translator's note.

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and second point gives the first equation for determining μ and ν. From (19) we can also find the relative fluctuation distribution of a pair of second points belonging to one first point. For the relative fluctuation distribution of a pair of first points we have

$$\rho(\vec{R}_{ik}) = \int \rho(\vec{R}_{ik}/\vec{R}_{1,1} \ldots \vec{R}_{q,q-1})\, \rho(\vec{R}_{1,1} \ldots \vec{R}_{q,q-1})\, d\vec{R}_{1,1} \ldots d\vec{R}_{q,q-1}, \tag{21}$$

where the conditional distribution for the given second points positions is once again determined on the basis of James' general theory. The coincidence of the distributions of relative fluctuations of a pair of first points and a pair of second points gives the second equation for determining μ and ν. We find as a result

$$\mu = q-1-1/q, \quad \nu = 1/q \tag{22}$$

Substituting (22) in (20) and integrating, we find the value of the parameter of the distribution of fluctuations of a network point in the second approximation:

$$Z = n(q-1)^{-2}[(q-1)^2+1]. \tag{23}$$

It is not possible to compare (33) with the formula given by James' [4] for a hexafunctional network, because (23) is based on the hypothesis that all the second points are different, while in the network taken by James some second points coincide. Comparing (23) with $Z = n(q-1)^{-1}$, which was obtained in (7) we see that the convergence of our method of approximations becomes more rapid as q increases. The value of the distribution of the relative fluctuations of the first points coincides with that given by formula (18) when $i=n$; $k=n$. It may be concluded from this that formulae (17) and (18), deduced in the first approximation, are true in the second also.

To find parameter Z_i for an arbitrary segment of the network (i is the number read off from the nearest point) we shall use the formula derived by James and Guth [8] which, for this particular case, takes the form

$$Z_i = Z + \frac{i(n-i)}{n}\left(1 - \frac{Z_{0n}}{n}\right), \tag{24}$$

where Z_{on} is the parameter of fluctuations of the end of the chain relative to the beginning, this parameter being equal, from (17), to $2n/q$.

To facilitate calculation of Q_2, we shall introduce a single-parameter interpolation formula which, for a pair of segments belonging to one or neighbouring chains, will approximate formulae (17) and (18), while when the distance between segments increases it will tend towards a limit equal to $2\bar{Z}$, where

$$\bar{Z} = \frac{1}{n}\int_0^n Z_i di = Z + \frac{n}{6}\left(1 - \frac{2}{q}\right) - \tag{25}$$

is the mean value of the parameter of fluctuations of a segment of the network. We propose as such a formula

$$Z_{ik}=2\bar{Z}\,[1-\exp(-\gamma\xi_{ik})]\,, \tag{26}$$

where ξ_{ik} is the number of segments, divided by n, which it is necessary to pass to move around the network along the shortest path from segment i to k, and

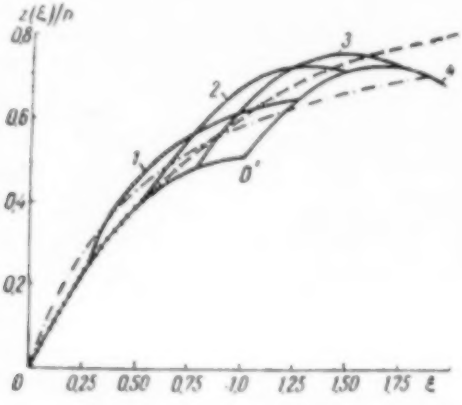

FIG. 2. $Z(\varrho)/n$ graphs from formulae: (17), (18), (27) and (29). Unbroken lines: (OO') from formula (17); (1, 2, 3, 4) from formula (18) when $k/n=0{\cdot}25$; 0·5; 0·75; 1; dashes – from formula (27); dashes and dots from formula (29).

where γ is the parameter determined from the condition of the best approximation of (26) to (17) and (18) in the region of change of the latter. It can be seen from Fig. 2 that for the case of a tetrafunctional network formula

$$Z_{ik}=0{\cdot}9n\,[1-\exp(-1{\cdot}1\xi_{ik})] \tag{27}$$

approximates satisfactorily to (17) and (18).

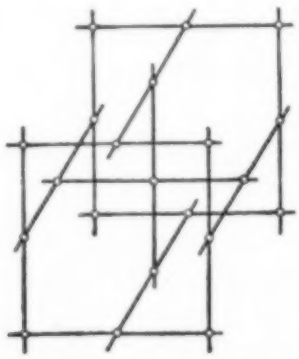

FIG. 3. Elementary cell of a cubic tetrafunctional network (showing mean positions of chains and points).

James [4] proposed for a cubic network an interpolation formula of the form

$$Z_{ik}=2Z\bar{\xi}_{ik}(\gamma+\bar{\xi}_{ik})\,. \tag{28}$$

However, as Fig. 2 shows,

$$Z_{ik}=0{\cdot}9n\bar{\xi}_{ik}/(0{\cdot}55+\bar{\xi}_{ik}) \tag{29}$$

approximates to (17) and (18) worse than (27). The root mean square error of formula (29) is 20 per cent more than the error given by formula (27). And, as for large $\bar{\xi}_{ik}$ the difference between (26) and (28) is less than the interpolation inaccuracy, formula (28) has no advantages over (26).

THE CUBIC TETRAFUNCTIONAL NETWORK IN THE LINEAR APPROXIMATION

Calculation of Q_2 for a real disordered network is an extremely complex task, because we need to know the distribution functions of $N(r)$ and $W_2\,(r,Z)$, and in its current form the network theory gives no way of finding these functions. We shall, therefore, calculate Q_2 for the correct cubic network often used in works on the theory of high-elastic deformations, which, as James and Guth [4,8] showed, gives in the case of non-interacting chains in a Gaussian approximation, the same law of deformation as a real network. By a cubic tetrafunctional network we mean a network in which from each point there come 4 chains consisting of n segments, a third of all the chains being directed along axis x, a third along axis y and a third along axis z. The direction of a chain means the mean direction of the vector uniting the ends of the chain. An elementary cell of such a network is shown in Fig. 3. A tetrafunctional network represents a certain averaging of a real network, and it must therefore be expected that calculation of a cubic network will give a result agreeing qualitatively and in order of magnitude with the result of calculating a real network. Of course, no quantitative agreement is to be expected, because Q_2 depends heavily on the form of the distribution functions. Thus, for example, in (3) it is noted that if $N(r)=v^{-1}$ and $W_2(r,Z)=\delta(Z-2\bar{Z})$, then Q_2 will not depend in any way on the deformation variables.

We shall further assume that a network without interaction is Gaussian, i.e., we shall take for $P(i,k)$ expression (3), which is rewritten in the form

$$P\,(i,\,\mathrm{k})=\left(\frac{3}{2\pi Z_{ik}a^2}\right)^{3/2}\exp\left[-\frac{3\,(\lambda_1^2x_{ik}+\lambda_2^2y_{ik}^2+\lambda_3^2z_{ik}^2)}{2Z_{ik}a^2}\right], \tag{30}$$

where x_{ik}, y_{ik} and z_{ik} are components of the vector uniting the mean positions of the i-th and k-th segments in the un-deformed state. For Z_{ik} we shall use formula (27).

The Gaussian approximation is inapplicable to very near segments, i.e., to segments for which $\bar{\xi}_{ik}\ll 1$. It will, however, be shown below that this area is not great for calculations of Q_2.

A cubic network consists of linear networks passing through the entire test-piece. We shall term these networks x_i—linear ($x_1=x$, $x_2=y$, $x_3=z$) in dependence on which of the coordinate axes are parallel to the direction of the chains of this network.

We shall write

$$Q_2=Q_2^{(1,1)}+Q_2^{(2,2)}+Q_2^{(3,3)}+Q_2^{(1,2)}+Q_2^{(1,3)}+Q_2^{(2,3)}, \tag{31}$$

where $Q_2^{(p,s)}$ denotes that part of the segment pairs sum in which the i-th segment belongs to an x_p-linear network, and the k-th to an x_s-linear network.

$Q_2^{(1\cdot2)}$ will have the form

$$Q_2^{(1,2)}=\frac{2G}{3}\sum_{i=\varepsilon}^{\infty}\sum_{k=-\infty}^{\infty}\sum_{\mu=-\infty}^{\infty}P(i,k,\mu). \tag{32}$$

Here G is the number of chains in the network and $p(i,k,\mu)$, from (30), has the form

$$P(i,k,\mu)=(0{\cdot}6\pi na^2)^{-3/2}[1-\varkappa(i,k,\mu)]^{-3/2}\exp\left\{-\frac{g(\lambda_1^2i^2+\lambda_2^2k^2+\lambda_3^2n^2\mu^2)}{n^2[1-\varkappa(i,k,\mu)]}\right\}, \tag{33}$$

where, according to (27), $\varkappa(i,k,\mu)=\exp[-1{,}1(|i|+|k|+|n\mu|)/n]$ and $g=\hbar^2/0{\cdot}6na^2$, and i is the number of the segment in the x-linear network, k in the y-linear, and μ the number of the plane in which the y-linear network lies. To satisfy the condition $i\neq k$ in determining Q_2, summing by i is done from some $\varepsilon\sim1$. For $Q_2^{(1\cdot1)}$ we have

$$Q_2^{(1,1)}=\frac{Gn}{3}\sum_{k=\varepsilon}^{\infty}\sum_{s=0}^{\infty}\sum_{|\mu_1|+|\mu_2|=2s}P(k,\mu_1,\mu_2). \tag{34}$$

Here $P(k,\mu_1,\mu_2)$ has a form similar to (33), k is the number of the segment in the x-linear network and the pair of whole numbers μ_1 and μ_2 determines the x-linear network.

The remaining terms in (31) are obtained from (32) and (34) by cyclic permutations.

Because $1/n\ll1$, in (32) and (34) summing with respect to i and k may be replaced by integrating. The function P for all the three arguments equal to zero has a pole of the order of 3/2. The integral (32) is a constant function of ε on the circumference of $\varepsilon\geqslant0$. When $\varepsilon=\mu_1=\mu_2=0$ integral (34) diverges. The final expression for the stresses will include only derivatives of $\partial Q_2/\partial\lambda_i$. When $\mu_1=\mu_2=0$ $Q_2^{(1,1)}$ depends only on λ_1. The derivative $\partial P(k,\mu_1,\mu_2)/\partial\lambda_1$ has, when $k=\mu_1=\mu_2=0$ a pole of the order of 1/2, i.e., when calculating $\delta Q_2/\delta\lambda_1$ we can place $\varepsilon=0$. It also follows from this that the area of small distances between segments is inessential in calculating Q_2.

The integrals in (31) may be found by methods of numeral integration. But at not very great g they may be expressed in the form of fairly rapidly converging series. For this we must place in (31) the series

$$P(i, k, \mu) = (0{\cdot}6\pi n r^2)^{-3/2} e^{-d} \sum_{l=0}^{\infty} \sum_{s=0}^{l} C_{ls} (-d)^s b^l ,$$

where

$$C_{ls} = \frac{(2l+1)!}{4^{l-p}(2p+1)!(l-p)!} ; \quad b = (|i| + |k| + |n\mu|)/n ; \qquad (35)$$
$$d = (\lambda_1^2 i^2 + \lambda_2^2 k^2 + \lambda_3^2 n^2 \mu^2)/n^2 ,$$

after which integration is elementary.

The conditional stress f (related to a unit of cross-section of an undeformed test-piece) in one-dimensional expansion we write in the form

$$f = f_0 (1 - \zeta J) , \qquad (36)$$

where f_0 is the stress calculated from the formula of the theory of non-interacting chains, the parameter ζ is determined in the second section, J_0 is the function from the multiplicity of expansion and the parameter g, which is determined after substitution of (31) in (1) and calculation of the stress.

Fig. 4 shows the results of calculations of function J in dependence on λ^{-1} for 4 values of parameter g. The selected g values correspond to

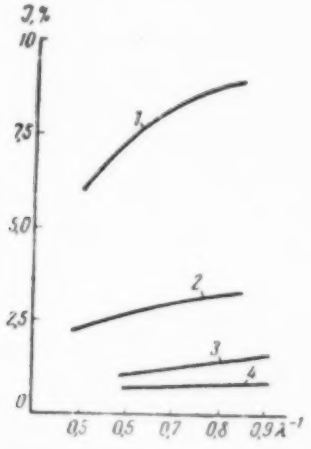

FIG. 4. Relationship between J and λ^{-1}. J is expressed in per cent values of $\sqrt{g}$ by the curves. (1) 1·5, (2) 2·0, (3) 2·5, (4) 3·0.

swelling degree ratios 1:0·42:0·22:0·125. We see that J decreases both during swelling and as λ increases, in quantitative agreement with experimental findings. It must be noted, that at small g values quantitative agreement is not obtained. As is shown in [3] the magnitude of ζ is equal to several units, and therefore the condition of the smallness of correct of the first approximation as compared to the zero term is satisfied.

CONCLUSIONS

The proposed expansion of the free energy of a network is good in the case when correlations between the relative fluctuations of a pair of segments decrease fairly rapidly as the distance between them increases. It has been shown in a particular example that such a decrease takes place.

2. For sufficiently soft rubbers it is possible to attain degrees of swelling such that the free energy expansion parameter is small, the Gaussian approximation for a network without interaction remains valid.

3. Calculation of a cubic tetrafunctional network in the linear approximation shows that even at high degrees of swelling the correction induced by volume effects makes a considerable mark on the deformation relationship.

4. The results obtained give grounds for hoping that taking into account the effect of excluded volume may explain the divergence between current theory and experiment.

In conclusion, I should like to thank Professor G. M. Bartonev for his interest and attention, and O. B. Ptytsyn for a number of valuable comments.

Translated by G. ELLIOT, M. SARGENT

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THE EFFECT OF AMINES ON THE STEREOSPECIFIC POLYMERIZATION OF PROPYLENE*

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GREAT strides have been made in recent years in the stereospecific synthesis of polymers based on α-olefines characterized by a regular structure of the molecular chain. The process takes place by means of catalytic complexes obtained by mixing with organometallic compounds halides of metals with transition valences. A component part of the complex catalyst is its solid surface, the properties and composition of which affect considerably the trend of the polymerization process. This, and a number of other characteristics besides, permit the detection of many essentially general features of the interaction mechanisms operative in heterogeneous stereospecific polymerization under the action of complex catalysts, and of other catalystic reactions taking place on the solid surface. Analogy with heterogeneous catalysis leads to the assumption that the introduction of various additives capable of reacting with at least one of the components in the catalytic system will affect the properties of complex stereospecific polymerization catalysts.

Unfortunately at the moment, the literature contains very little information pertaining to examination of the effect of specially selected additives on the properties of the catalytic system and the trend of the process. At the same time the importance of these factors is conclusively demonstrated on many examples of the heterogeneous catalysis of other chemical processes.

We considered it convenient to study the influence of nucleophilic organic compounds (according to Lewis) capable of interacting with both components of the catalytic system [1–4] and, in particular, that of amines on the stereospecific polymerization of propylene. A study of the behaviour of the Ziegler-Natta heterogeneous catalytic system during stereospecific polymerization with the introduction of additives may facilitate a deeper understanding of the elementary processes involved in this reaction.

The literature includes but a single communication dealing with the polymerization of hexene-1 in the presence of the catalyst system $TiCl_4$ (20 mmol) mixed with Al (*iso*-C_4H_9)$_3$ (10 mmol) where an inhibiting action of triethylamine is revealed [5]; 2 mmol of the latter inhibited polymerization but this was restarted by the introduction of a fresh portion of the catalyst.

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We performed experiments on the polymerization of propylene in 4-l. metallic reactors at 60°C for 10 hr over the catalyst system $Al(C_2H_5)_3+TiCl_3$ (molar ratio 3:1) in a saturated hydrocarbon medium. The amines were added in different ratios relative to the titanium trichloride and the order in which the catalyst components and the amine were added had no noticeable effect on the experimental results. Mainly we added the amines to the ready-made mixture. The results of a number of experiments on the influence of triethylamine, diphenylamine, aniline and dimethylaniline on the stereospecific polymerization of propylene are listed in table 1.

TABLE 1. POLYMERIZATION OF PROPYLENE IN THE PRESENCE OF AMINES

No. of expt.	Molar ratio $\frac{\text{amine}}{TiCl_3}$	Mol. wt. of polymer	Yield (g)	No. of expt.	Molecular ratio of $\frac{\text{amine}}{TiCl_3}$	Mol. wt. of propylene	Yield (g)
Donor electrons — aniline				Donor electrons — triethylamine			
1	—	67,200	287	17	—	53,600	335
2	0·5	124,000	288	18	—	65,000	278
3	1	168,000	251	19	0·5	117,000	278
4	1	168,000	260	20	0·5	113,000	225
Donor electrons — diphenylamine				21	1·0	156,000	283
				22	1·0	156,000	380
5	—	77,800	—	23	1·7	124,000	342
6	—	63,400	300	24	4·0	98,000	200
7	0·35	117,000	—				
8	0·4	124,000	398	Donor electrons — dimethylaniline			
9	1·0	156,000	218	25	—	53,600	335
10	1·0	180,000	246	26	—	65,000	268
11	1·15	166,000	374	27	0·5	98,400	278
12	2·2	78,000	—	28	1·0	120,000	339
13	2·2	62,400	—	29	1·0	112,000	300
14	2·2	72,800	56·6	30	2·0	111,000	—
15	3·8	85,600	76·6	31	4·0	100,000	90
16	6·7	72,800	116	32	4·0	105,500	114

The Table shows that as the amine: titanium chloride ratio increases to 1 an abrupt rise in molecular weight takes place (by a factor of 2–3) giving the normal polymer yield (Expts. 1–10, 17–22 and 25–29). With an excess of the amine the molecular weight of the polypropylene decreased and with it the yield of the product (Expts. 11–16, 23–24, 30–32). As can be seen the maximum molecular weight under the conditions of the experiment occurred for an amine: titanium chloride ratio of 1:1. On the face of it this maximum may be ascribed to the formation of a complex of analogous composition and more readily polymerizable. Hence changes could be anticipated in the proportion of the elementary

chain growth and termination processes. An increase in the chain growth rate and a decrease in the probability of chain termination should result in higher molecular weight of the polymer. In this connexion it is relevant to determine the composition and study the polymerizability of the interaction products of titanium trichloride and amine obtained for different ratios of the starting components. Only one similar complex is known having the composition $2(CH_3)_3N$-$TiCl_3$ (1) which was obtained by the forward reaction of $TiCl_3$ with trimethylamine in a liquid amine medium. The interaction of titanium trichloride with amines in an unsaturated hydrocarbon medium was studied for amine: titanium chloride ratios ranging from 0.5 to 10 at 20 and 60°C. The starting components were mixed in a glass reaction vessel for 3 hr then the precipitate filtered off at the temperature at which the complex had been prepared, thoroughly washed with petroleum ether to eliminate the excess amine, and weighed. All operations were accomplished under dry nitrogen. The composition of the complex was determined from the molar ratio based on analyses of the precipitates.

Figure 1 plots the composition of the complex as a function of the starting ratio amine : titanium trichloride in the reaction mixture. It reveals a complex of composition 1:1 occurred only with a considerable excess of amine in the reacting mass relative to the titanium trichloride (about twice as much). Consequently, irrespective of the ratio of the components, the titanium trichloride

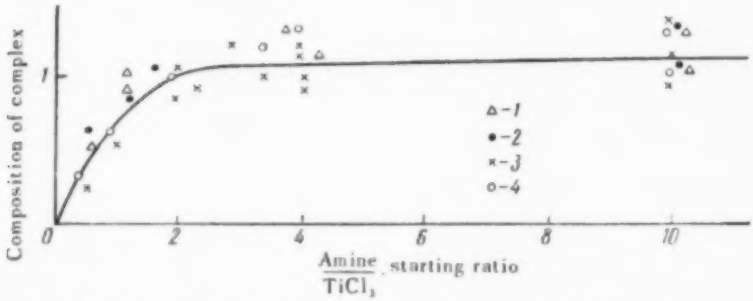

FIG. 1. Composition of precipitate as a function of the amine: titanium chloride ratio. Aniline: (1) 20°C, (2) 60°C; Triethylamine: (3) 20°C, (4) 60°C.

does not take all the amine from the solution. Free amine was invariably present in the filtrate. Analogous results were found by titrating the prepared precipitates with diphenylpicrylhydrazyl; the ability of the latter to change the colour of the solution from violet to yellow on interacting with $TiCl_3$ was turned to account (Fig. 2, curves 1 and 2). It can be seen that the maximum area occupied by the amine occurred with a starting molar ratio of amine : titanium chloride equal to two and more.

Since the stereospecific polymerization of propylene was conducted in the presence of triethyl aluminium, and the experimental results from analysis of

the precipitates showed that with a 1:1 starting ratio of amine : titanium chloride, 40–60 per cent of the original titanium (Fig. 2) interacts, it was natural to assume that the remaining $TiCl_3$ reacted with the triethyl aluminium. Precipitates were

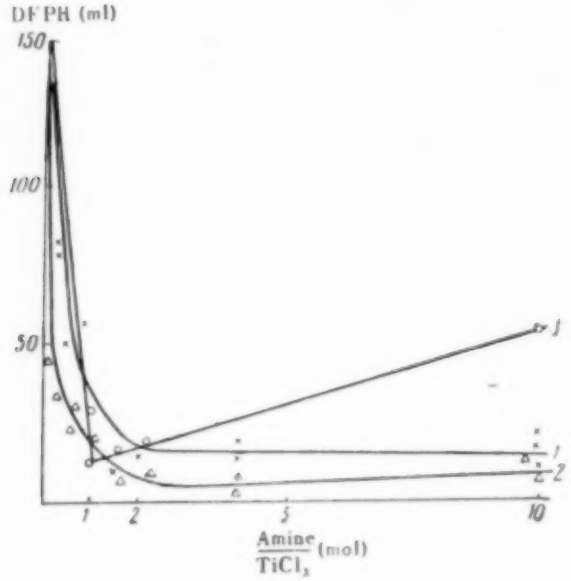

FIG. 2. Plots for titration of precipitates with α,α-diphenyl-β-picrylhydrazyl (DFPH). (1) $TiCl_3$ + triethylamine; (2) $TiCl_3$ + dimethylaniline; (3) $TiCl_3$ + triethylamine + triethyl- aluminium.

prepared by mixing titanium trichloride and amine in a dry, saturated hydrocarbon medium (*n*-heptane, benzine) with the subsequent addition of triethyl aluminium in a 3:1 ratio with titanium trichloride.

Figures 2 and 3 show, in common with expectations, that the minimum on the titration curve was displaced to the left and occurred for a starting molar ratio of amine : titanium trichloride of the order of 1:1. Moreover, in the precipitates prepared by mixing titanium trichloride, triethylamine and triethyl aluminium in the ratio 1:2 : (0·5–3·5), a considerable quantity of aluminium occurs (from 3·1 to 5·2 per cent and moreover a decrease took place in the content of nitrogen down to 1·58 per cent) (determined by Kjeldahl's method) and in that of the titanium trichloride down to 10·2 per cent (titration with ammonia ferric alum).

$TiCl_3 \cdot (C_2H_5)_3N$. Calculated in % : N 5·5 ; Ti^{+3} 19.

It should be noted that neither the precipitates formed by mixing titanium trichloride and amine nor the ones obtained by mixing titanium trichloride, amine and triethyl aluminium caused the propylene to polymerize. Yet, on addition of a

fresh portion of triethyl aluminium to these precipitates, the resulting catalyst system readily induced stereospecific polymerization which, under the given conditions, resulted in a sharp increase in the molecular weight of the polymer. Most likely the increase in the, molecular weight of the polypropylene with a 1:1 starting ratio of amine : titanium chloride in the reacting mass (Table 1) is unrelated to the formation of a complex of analogous composition and is merely an apparent coincidence. Invariably, regardless of the starting ratio of the components, the liquid phase contains free amine that readily interacts with the triethyl aluminium to form corresponding complexes [3–5]. This may lead to lower probability of chain rupture on the triethyl aluminium [6] and, consequently, to a rise in the molecular weight of the polymers. The inhibiting action of the amines when in excess can be explained by the fact that the free triethyl aluminium present in solution is then more thoroughly bound. Here the complete absence of free triethyl aluminium in the filtrate has been demonstrated by means of the indicator methyl violet [7].

However, sight must not be lost either of a probable promoting influence of the amines, which will bring about a change in the relationship between the elementary chain growth and termination processes. In a number of experiments (mainly involving halide-substituted amines) an increase occurred in the over-all propylene polymerization rate. A point to bear in mind, and one which also emerges from the results listed in the Table, is that the screening of part of the surface of the catalyst complex by the amine (to a given level) did not reduce the total polymer yield. An electron pair of an amine donor molecule is capable of interacting with the α-shell of the titanium trichloride to form corresponding bonds [1], and this must be reflected in the electron state of the adsorbed organometallic molecule and thus in the energy of the active bond as well. On the magnitude of the latter depends both the rate of the elementary growth reactions and also the probability of a rupture at the active bond.

Many theories have been formulated to account for the mechanism of stereospecific polymerization [8] of which essentially two predominate; these state that the double bond of the monomer may interact in the radical or polar form. The promoting action of amines as bases according to Lewis is characteristic for anionic polymerization [9].

EXPERIMENTAL

Propylene was polymerized for 10 hr in 4 l metallic reaction vessels [10] at 60°C. The vessels were charged with 500 ml of a 4% solution of triethyl aluminium in a saturated hydrocarbon (*n*-heptane, benzine), 8·3 g of titanium trichloride, and, after mixing for 10 min, the appropriate amount of amine was added; then after 15 min 400 g of propylene were introduced.

The precipitates were prepared in three-necked vessels of 0·05–0·5 l. capacity under pure nitrogen. A calculated amount of amine was added dropwise

for 30 min to a weighed portion of $TiCl_3$ in dry heptane. After thorough stirring for 3 hr, the precipitate was filtered off at the preparation temperature of the complex, washed for 4 hr with petroleum ether, dried in a current of nitrogen, and weighed. The reaction was attended by a change in the colour of the precipitate and its spontaneous granulation to form particles some tens of microns in size. The precipitate was analyzed for its content of nitrogen [11], chlorine [12] and Ti^{+3} [13].

The precipitates were titrated with a solution of α, α-di-phenyl-β-picrylhydrazyl in *n*-heptane (0·1375 g/l.).

CONCLUSIONS

(1) The stereospecific polymerization of propylene was conducted in the presence of nucleophilic additives (amines). It was shown that the molecular weight of the polymer changes as a function of the amine: titanium trichloride ratio.

(2) The pricipitates formed by mixing amine with titanium trichloride and amine with titanium trichloride and triethyl aluminium were examined and their catalytic activity during polymerization studied.

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THE THERMAL OXIDATIVE DEGRADATION OF POLYPROPYLENE–I. OVER-ALL CHARACTERISTICS OF THE OXIDATION REACTION*

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THE thermal oxidative degradation of polypropylene has not been studied hitherto. In the literature we have found only references to a patent [1] which describes the preparation with hydrogen peroxide of polypropylene and a number of other vinyl polymers. Since polypropylene is starting to grow in practical importance its oxidation must be studied because of its great bearing on the appropriate choice of antoxidants effective under a variety of conditions.

The present paper reports the first experimental results that were obtained by studying the oxidative degradation of polypropylene over the temperature range from 120–150°C.

PROCEDURE

For the experiments on the oxidation of polypropylene a simple static apparatus was utilized which is schematically represented in Fig. 1. The reaction vessel 1, was charged with a 50 mg weighed portion of fine polypropylene powder. A constant temperature was maintained in this vessel by means of a double-

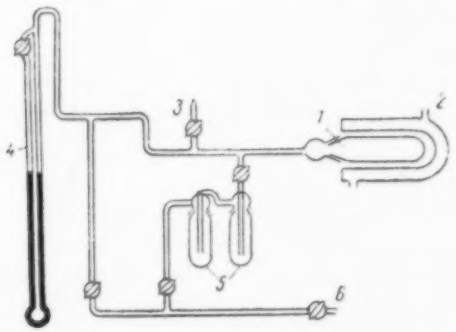

FIG. 1. Apparatus for studying the oxidative degradation of polypropylene. (1) Reaction vessel; (2) Tube to ultrathermostat; (3) Tube to vessel containing oxygen; (4) Mercury manometer; (5) Traps; (6) Cock to vacuum pump.

* Vysokomol. soedin. 1: No. 11, 1696–1702, 1959.

walled glass reservoir into which flowed hot liquid from an ultrathermostat via tube 2. Prior to the experiment the weighed portion of the polymer was kept for 2 hr *in vacuo* at 150°C to eliminate traces of dissolved gases and vapours contained in the polymer. The low pressure polypropylene chosen had a mean molecular weight of about 200,000, an ash content of 0·7 per cent and melted at about 153°C. After removal of the volatile substances oxygen was passed into the reaction vessel via cock 3, until a given pressure was attained. In the greater part of the experiments the starting oxygen pressure was 500 mm. Pressure changes in the reaction vessel were recorded by the mercury monometer 4. The products were analyzed at various intervals during the course of the reaction and for this purpose were passed into traps cooled by liquid nitrogen.

Carbon dioxide was dissolved in baryta water. Carbon monoxide was oxidized by iodine pentoxide and the resulting carbon dioxide converted to $BaCO_3$. The CO_2 was separated from the barium carbonate and its volume measured in a gas burette.

Aldehydes were dissolved and determined polarographically on a ground of 0·1 N LiOH [2]. On completion of the experiment the apparatus was evacuated via cock 6.

Inhibitors were added to the polypropylene either by thoroughly pulverizing in a mortar a mixture of the polymer and a weighed portion of inhibitor, or by dissolving in hot toluene followed by evaporation of the solvent on plane glass to produce a film. The solid organic peroxide was dissolved in ether and powdered polypropylene added with stirring. The ether was then driven off at decreased pressure.

EXPERIMENTAL RESULTS

We studied the oxidative degradation of polypropylene at 120, 130, 140 and 150°C and a starting oxygen pressure of 500 mm. Curves showing the fall in pressure on oxidation of polypropylene are plotted in Fig. 2. It will be seen that the reaction has a marked induction period τ of the order of some tens of minutes when the oxygen absorption rate is extremely low. With increasing temperature the induction period decreases. We further studied the influence of several additives on the kinetics associated with the oxidation of polypropylene. The experiments which were conducted with additions of *n-tert* butylcumene revealed that additions of hydrogen peroxide reduced the induction period.

Figure 3 gives the experimental curves for the oxidation of polypropylene at 140°C in the presence of various amounts of hydrogen peroxide.

We found the following empirical relationship between the induction period and the concentration of hydrogen peroxide

$$\tau = \tau_0 - a\sqrt{C}\,. \qquad (1)$$

where τ_0, induction period in absence of peroxide, C, concentration of added peroxide, a, constant.

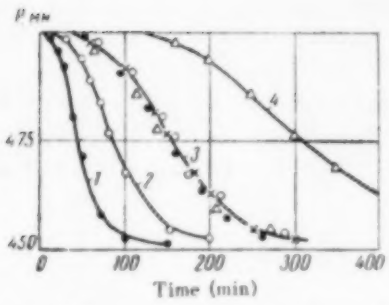

FIG. 2. Fall in pressure on polypropylene oxidation. Curves 1–4 correspond to temperatures of 150; 140, 130 and 120°C respectively.

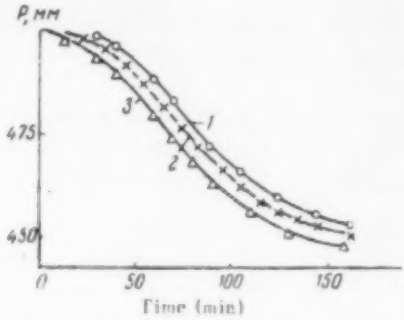

FIG. 3. The same in the presence of *n-tert*-butylcumene hydroperoxide at 140°C. Curves 1–3 correspond to experiments with the addition of 0; 0·5 and 1 per cent peroxide.

The dependence of the induction period on the concentration of added peroxide is plotted in Fig. 4 against coordinates τ and $\sqrt{C}$. It follows from the Fig. that this dependence is well described by equation [1].

In addition we examined the effect of inhibitors on the rate of oxidation of polypropylene: for this purpose varying amounts of oxidation inhibitors were added to a weighed sample of polypropylene.

Figure 5 for instance gives the kinetic curves for the oxidation of polypropylene in the presence of different amounts of diphenylolpropane. It shows that the induction period increases directly with the concentration of inhibitor introduced.

Besides diphenylolpropane we also added to polypropylene other inhibitors in varying concentrations. The addition of 3% N, N′ and β,β'-naphthyl-*p*-

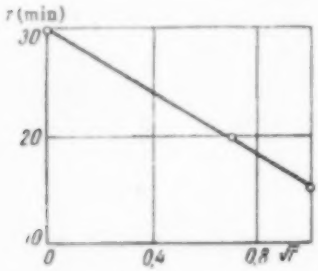

FIG. 4. Induction period as a function of peroxide concentration at 140°C against coordinates τ and $\sqrt{C}$.

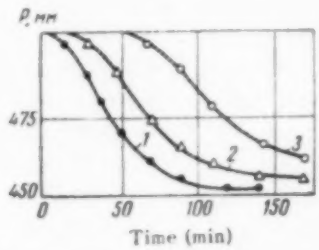

FIG. 5. Fall in pressure on oxidation of polypropylene in the presence of diphenylolpropane at 150 °C. Curves 1–3 relate to experiments with additions of 0·1 and 5 per cent inhibitor.

phenylenediamine at 150°C and an oxygen pressure of 500 mm extended the induction period from 10 to 50 min. The other inhibitors tested increased the induction period to a lesser degree.

In the reaction products of polypropylene oxidation extracted at various intervals we found water, formaldehyde, acetaldehyde, carbon monoxide and dioxide.

The results obtained from polarographic determinations of the aldehydes are plotted in Fig. 6. The Fig. shows that during the first 50 min of the reaction the aldehydes are slowly accumulated, after which the amount of accumulated

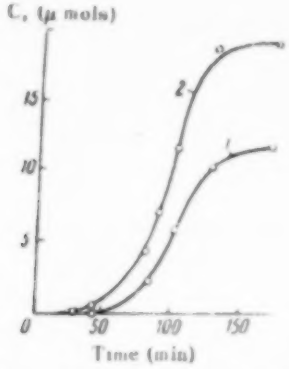

FIG. 6. Accumulation of formaldehyde (1) and acetaldehyde (2) on oxidation of polypropylene. $P_0 = 500$ mm, $T = 150°C$.

aldehydes quickly rises and approaches the limiting value on termination of the reaction. For formaldehyde this limiting value is 12 μM, and for acetaldehyde, 18 μM.

It will be obvious that the maximum concentration of aldehydes does not correspond to the maximum rate of polypropylene oxidation. Thus it was possible to conclude that aldehydes are not the substances that participate in degenerative branching.

In order to check this conclusion experimentally we accomplished a series of experiments on the oxidation of polypropylene, introducing into the reaction vessel amounts of acetaldehyde ranging from 1 to 5 mm. These experiments proved that the addition of acetaldehyde scarcely affects the kinetics of polypropylene oxidation.

A number of authors [3,4] maintain that the degenerative branching occurring on the thermal oxidative degradation of polymers such as polyethylene is associated with decomposition of the hydrogen peroxide.

With a view to verifying this point we tried to detect hydrogen peroxide in solid, partly oxidized polypropylene. Our method was to treat powdered polypropylene with an acidified solution of KI after it had been oxidized at 150°C for various periods of time (from 10 to 100 min). The reaction was performed in the absence of oxygen for 30 min. In all cases free iodine was liberated and titrated with hyposulphite.

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The maximum amount of hydrogen peroxide—12 μM—was found in polypropylene that had been oxidized for 50 min, i.e. the time coinciding with the maximum rate of oxidation.

Determination of CO_2 and CO at various intervals disclosed that the accumulation of the oxides of carbon takes place by the same mechanism as the accumulation of the aldehydes. Initially CO_2 and CO are accumulated slowly, then the rate increased sharply. On completion of the reaction 60 μM of CO_2 and 120 μM of CO had accumulated. The oxides of carbon are evidently by-products of the process formed by the oxidation of the aldehydes similar to the case with the oxidation of hydrocarbons in the gaseous phase at high temperature [5].

The IR absorption spectrum of the starting polypropylene revealed that it contained a negligible number of carbonyl groups. In a sample of polypropylene that had been oxidized at 150°C and under an oxygen pressure of 500 mm for 30 min the absorption band corresponding to the carbonyl group had increased by some factors of 10. Moreover, absorption maxima were clearly discernible at 1715 and 1725 cm^{-1} and these would seem to be attributable to the presence of ketone and aldehyde groups in the oxidized polypropylene.

DISCUSSION

The kinetic curves for the fall in pressure inside the reaction vessel during the initial stages of the process are well described by Semenov's equation [6] for chain reactions with degenerative branching:

$$-\Delta p = Ae^{\varphi t}. \tag{2}$$

With increasing temperature the autocatalysis factor φ steadily grows and this results in a faster pressure decrease. In a first approximation the value

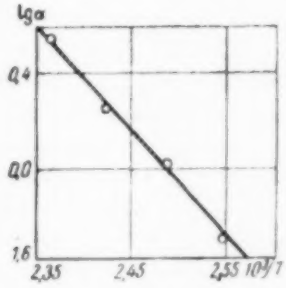


FIG. 7. Conversion coefficient as a function of temperature against coordinates lg α and $1/T$.

of A may be considered constant. If with increasing temperature the value of φ rises by a factor of α, we shall obtain, by reducing the time scale by the same factor

$$\varphi t = idem\ . \tag{3}$$

and the curves described by formula [2] coincide at different temperatures. Such a superposition of curves is exemplified by the kinetic curve at 130°C in Fig. 2. By choosing conversion coefficients for the time scale $\alpha=\varphi/\varphi_0$ where φ_0 refers to the basic curve, all our curves coincided with curve 3. The results of the superposition are shown by dots, crosses and triangles. It will be clear that the temperature dependence of the coefficients α gives the temperature dependence of the autocatalysis factors φ.

In Fig. 7 the experimental points characterizing the temperature dependence of α are plotted against the co-ordinates lg α and $1/T$. The points fall practically on a straight line from the slope of which we found the effective activation energy of 22,000 cal/mol. Hence, at $p=500$ mm, φ accordingly depends upon temperature:

$$\varphi = ae^{-22{,}000/RT}. \tag{4}$$

The chain-like nature of the polypropylene oxidation process was confirmed by experiments involving the addition of hydrogen peroxide and inhibitors. Substances that produce active radicals, e.g. peroxides, accelerate the reaction: against this, substances which capture the radicals retard the reaction.

From the relationship established between the induction period and the concentration of added hydrogen peroxide it could be concluded that scission of the chain during oxidation of polypropylene takes place owing to the recombination of pairs of radicals.

Our experiments demonstrated that initiation, growth, rupture and branching occur predominantly in the solid phase. Since peroxides are found in the solid phase it may be assumed, on analogy with the known facts about the oxidation mechanism of other hydrocarbons, that degenerative branching proceeds on decomposition of the hydrogen peroxide in the polypropylene which is evidently formed in the very early stages of the reaction.

This postulate accords with paper [1] in which hydrogen peroxide was obtained from polypropylene and a series of other vinyl polymers at 60–80°C where the hydrogen peroxide was probably the sole reaction product. At temperatures above 100°C it becomes likely that besides hydrogen peroxide, aldehydes will also be formed owing to decomposition of the peroxide radicals. It must, moreover, be assumed that the peroxide radical previously undergoes isomerization. The following is a possible way in which the aldehydes are produced. A peroxide radical is isomerized so that the C—C bond is ruptured ($\sim$80 kcal) and an O—C bond created ($\sim$90 kcal). Energetically this process is valid as has been demonstrated on the oxidation of propane [7].

Since the isomerization process is monomolecular, its rate is described by the equation:

$$w_1 = 10^{13}e^{-E_1/RT}(R), \tag{5}$$

where R=concentration of peroxide radicals.

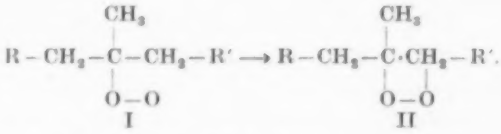
Since the process liberating hydrogen is bimolecular, its rate is

$$w_2 = f \cdot 10^{10} e^{-E_2/RT} (R) (M) , \tag{6}$$

where f = steric factor, M = concentration of molecules.

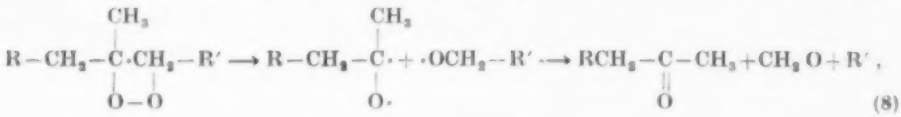
Taking for M the value 10^{22}, $f \simeq 10^{-3} - 10^{-4}$, $E_1 = 15$–20 kcal/mol and $E_2 \simeq 10$ kcal, we obtain for the ratio of the rates w_1 and w_2 a value low with respect to 1, i.e. the rate of both processes is of the same order.

Thus, a peroxide radical with a known degree of probability is isomerized in accordance with the scheme:



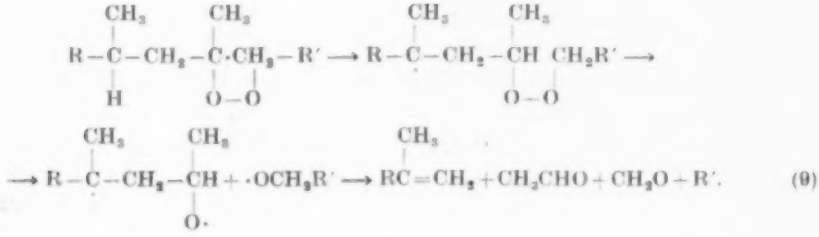
(7)

Next, in radical II, either the O—O bond is ruptured, forming formaldehyde



(8)

or else further isomerization takes place attended by the migration of a hydrogen atom and decomposition, resulting in the formation of acetaldehyde and formaldehyde:



(9)

Apart from this method the formation of a certain amount of aldehydes is possible on decomposition of peroxide. The rate of aledhyde formation by both methods can be determined approximately. With decomposition of a peroxide radical, as demonstrated by Semenov [7], the limiting stage is isomerization of the radical at the rate

$$w_{\text{isom}} = 10^{13} e^{-20{,}000/RT} (\text{RO}_2) . \tag{10}$$

Suppose that with decomposition of peroxide the limiting stage is the formation of RO˙ and ˙OH radicals. The activation energy of the monomolecular decomposition of peroxide is of the order of 30–33 kcal. The rate of peroxide decomposition is then

$$w_{\text{decomp}} = 10^{13} e^{-30{,}000/RT} (\text{RO}_2\text{H}) . \tag{11}$$

The ratio of the rates w_{isom} and w_{decomp} at $T \simeq 400°C$ is

$$\frac{w_{isom}}{w_{decomp}} \simeq e^{-10,000/RT} \frac{(RO_2)}{(RO_2H)} \simeq 10^5 \frac{(RO_2)}{(RO_2H)}. \quad (12)$$

Assuming the concentration of (RO_2) to be 10^{-11}–10^{-16}, and of (ROOH) to be 10^{-5}–10^{-6}, the ratio (12) is close to unity. This rough calculation must be verified by direct experiments that will have to elucidate the actual part played by isomerization and decomposition of the peroxide radicals with thermal oxidative degradation of polypropylene.

In our experiments 0·25 μM of polypropylene (taking its molecular weight as 200,000) was subjected to oxidation, after which 12 μM of hydrogen peroxide groups were found in the reaction products. This implies that about 0·1 per cent of the tertiary carbon groups in the polypropylene molecule formed the hydrogen peroxide groups. At the same time the reaction products had accumulated some 30 μM of aldehydes and 180 μM of carbon oxides. Only further studies will permit an interpretation of the formation mechanism of these substances.

CONCLUSIONS

(1) It is shown that the character of the kinetics, and also the influence of additions of peroxides and inhibitors, indicate a chain-type thermal oxidative degradation of polypropylene.

(2) In the products of the polypropylene oxidation reaction H_2O, CH_3CHO, CH_2O, CO, CO_2 and peroxides occur.

(3) The kinetics associated with the oxidative degradation of polypropylene in the temperature range 120–150°C are studied and the effective activation energy of the process determined, i.e. $E = 22$ kcal/mol.

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THERMAL OXIDATIVE DEGRADATION OF POLYPROPYLENE—II. THE KINETICS OF THE INITIAL OXIDATION STAGE*

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THE study of the oxidative degradation of polypropylene at temperatures close to the melting point has a considerable practical bearing on the formulation of convenient methods to process this polymer. Furthermore, extrapolation of the findings to lower temperatures should yield information on the ageing process of polypropylene products about which little is known.

In common with the greater proportion of organic compounds polypropylene oxidizes by an autocatalytic mechanism [1, 2] at an initially very low rate. An extremely convenient rate characteristic for this process, therefore, is the induction period τ conventionally taken as the time from initiation of the reaction to a given point very soon after. In the initial reaction stage while the rate is low,the admission of oxygen to the site of the reaction exceeds its consumption owing to diffusion and the rate of the process is governed solely by chemical factors. At the end of the induction period the rate of oxidation very rapidly becomes constant, evidently depending only on the rate of diffusion of the oxygen into the interior of the substance, i.e. on the geometrical dimensions of the sample [3]. Consequently the problem of polypropylene stabilization is tantamount to extending the induction period of the oxidation process.

We studied the kinetics of the initial polypropylene oxidation stage at 120–150°C, using powdered polypropylene, with a melting point of 152°C, a mean molecular weight of about 200,000 and an ash content of 0·07 per cent. Technical-grade oxygen was washed with water; water and other impurities were frozen out by means of liquid air.

Oxidation was studied on a static apparatus. A cylindrical reaction vessel was charged with a weighed portion of the polypropylene, the air pumped out and the temperature raised to 140°C. The polypropylene was kept under these conditions for about 1 hr with continuous pumping to remove the volatile impurities, then the thermostat was adjusted to the required temperature and oxygen introduced into the reaction vessel. The reaction was followed by a decrease

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in oxygen pressure. Inasmuch as gaseous products form at an advanced stage polypropylene oxidation our method was reliable for just the initial stage.

Figure 1 gives specimen kinetic curves for the oxidation of polypropylene at 140°C, and they have a clearly marked autocatalytic character. We took the induction period conventionally as the time for which $-\Delta P = 1{\cdot}0$ mm Hg. A slight error in determining $-\Delta P$ little affects the accuracy of determining the induction period. As an instance, if the induction period for curve 2 is taken as the time corresponding to $-\Delta P$ values of 0·5 or 2·0 rather than 1·0 mm, the induction period is altered only 15 per cent.

Figure 2 plots the induction period against temperature and pressure. The Figure shows that at low pressures (below 150–200 mm Hg) the induction period τ grows strongly inversely with the pressure. For these pressures the reciprocal of the induction period $1/\tau$, proportional to the mean rate of the initial reaction stage, is directly proportional to the pressure ($1/\tau P_0 = \text{const.}$). At higher pressures the induction period alters little with pressure. The effective activation energy, com-

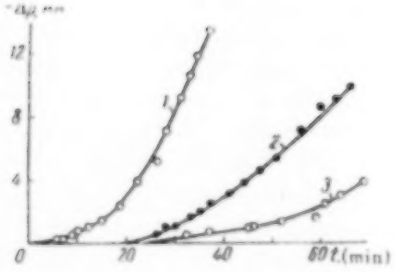

FIG. 1. Kinetic curves for the oxidation of polypropylene, $T = 140$°C; (1) $P = 588$ mm, (2) 146 mm, (3) 88 mm.

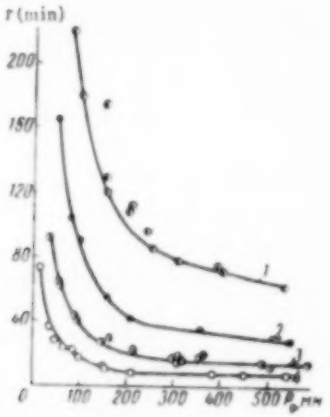

FIG. 2. Induction period of polypropylene oxidation as a function of temperature and pressure. (1) 120°C; (2) 130°C; (3) 140°C; (4) 150°C.

puted from the temperature dependence of the induction period, (more precisely, from $1/\tau P_0$, Fig. 3), was $26{\cdot}0 \pm 0{\cdot}5$ kcal/mol for pressures up to 100 mm Hg inclusive, and $22{\cdot}5 \pm 0{\cdot}5$ kcal/mol for a pressure of 500 mm Hg.

The first oxidation product of saturated hydrocarbons is hydrogen peroxide [2]. Our experiments disclosed that slightly oxidized polypropylene liberates iodine from a solution of potassium iodide acidified with acetic acid, viz. it contains peroxide compounds. The decomposition of hydrogen peroxide to forms free radicals initiates further oxidation of the polypropylene. If a reaction that has already started is terminated by pumping out the oxygen rather than by

decreasing the temperature, a considerable quantity is given off of gaseous products that have obviously been formed on decomposition of hydrogen peroxide. The rise in pressure attains 10–30 per cent of the complete drop in pressure occurring on oxidation and continues for 30–60 min at a rapidly decreasing rate. On repeated admission of oxygen the induction period arises again, increasing as a function of the time for which the reaction is interrupted (Fig. 4).

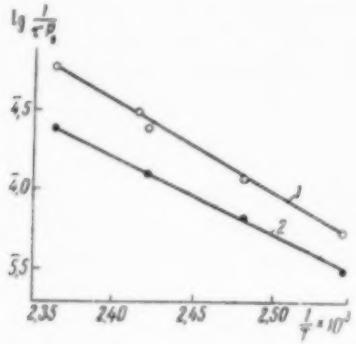

FIG. 3. $\lg \tau P_0$ as a function of the reciprocal of the temperature (1) for $P_0 = 100$ mm; (2) for $P_0 = 500$ mm.

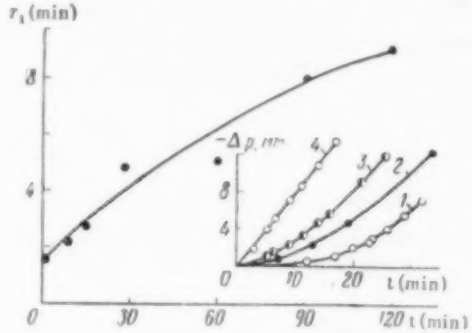

FIG. 4. Induction period on repeated admission of oxygen as a function of the period of interruption of the reaction, $T = 140°C$; $p = 300$ mm. Inset—specimen kinetic curves: (1) before interruption, (2) interruption 120 min, (3) 60 min, (4) 1 min.

In a special series of experiments (at 140°C) the reaction was initiated at a pressure of 97·5 mm Hg, involving an induction period $\tau_1 = 42$ min. During the induction period the pressure jumped to 300 mm Hg, equivalent to an induction period of $\tau_2 = 18$ min. Besides time t_2 was linearly proportional to t_1 from the

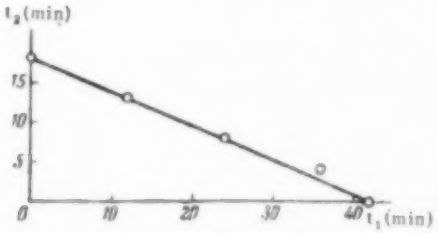

Fig. 5. Experiments on increasing pressure during induction period; (t_1) time from admission of oxygen to pressure rise, (t_2) time from pressure rise to end of induction period.

start of the pressure rise to the end of the induction period, and from the start of the experiment to the start of the pressure rise (Fig. 5), i.e. fulfilling the condition

$$\frac{t_1}{\tau_1}+\frac{t_2}{\tau_2}=1\,.$$

Consequently the same relationship of rate to pressure is preserved for any extension in the induction period.

Exposure of the polypropylene to direct sunlight beforehand (for about 5 hr) did not curtail the induction period. In the presence of water vapour ($P_{H_2O}=1$mm Hg, $P_{O_2}=300$ mm Hg) the induction period decreased some 20 per cent. Our experiments also showed that different polypropylene samples oxidize at dissimilar rates. The reason for this behaviour has not yet been elucidated.

CONCLUSIONS

(1) The initial oxidation stage of polypropylene is studied. The character of the relationship between the induction period and the pressure is elucidated.

(2) It is shown that on oxidation polypropylene forms unstable peroxide compounds.

(3) A series of experiments is conducted to study the induction period with varying oxygen pressure.

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COPOLYMERIZATION OF DIMETHYL AND METHYLPHENYLDIALLYLSILANE WITH PROPYLENE ON THE COMPLEX CATALYST $(C_2H_5)_3AL + TiCl_4$*

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THE feasibility of polymerizing unsaturated silicon hydrocarbons was established for the first time by Ushakov and Itenberg [1] with triethylvinylsilane. By treating triethylvinylsilane with conc. H_2SO_4 the authors obtained a low molecular, liquid polymer. In recent years the polymerization of alkenylsilanes with different structures has been studied by Petrov, Korshak and co-workers [2–7], Wagner [8], Curry [9, 10], Andrianov [11, 14] and others [12, 13]. These authors demonstrated the polymerization of alkenylsilanes over a wide range of temperatures and pressures (up to about 7,000 atm) in the presence of a variety of catalysts: platinized carbon, aluminium chloride, zinc chloride, boron fluoride etherates and peroxides.

The feasibility of polymerizing dialkyldiallylsilanes on the complex catalyst $(C_2H_5)_3Al + TiCl_4$ has previously been reported [15] where both liquid and crystalline polymers were obtained. Somewhat later Natta [16] reported the polymerization of trialkylalkenylsilanes in the presence of $(C_2H_5)_3Al + TiCl_4$ and $TiCl_3$. The polymerization of trimethylallylsilane yielded high-molecular linear polymers with melting points of 350–360°C.

A number of authors have studied the feasibility of copolymerizing alkenylsilanes with several unsaturated compounds. Hurd and Roedel [17] examined the copolymerization of vinyl and allylpolysiloxanes with vinyl acetate, styrene, methylmethacrylate, acrylonitrile and other unsaturated compounds in the presence of peroxide catalysts. They obtained copolymers (with methylmethacrylate, for instance) with excellent electrical insulating properties. Mackenzie [18] showed that tetra-allylsilane copolymerizes with vinyl acetate, methyl and butyl methacrylate to form products that are stable to solvents and high temperatures. Wagner and co-workers [8] studied the copolymerization of vinyltrichlorosilane and vinyltriethoxysilane with propylene, *iso*butylene, vinyl acetate, methyl methacrylate and other unsaturated compounds in the presence

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of peroxide catalysts. The authors observed great reactivity on the copolymerization of vinyltriethoxysilane relative to vinyltrichlorosilane. Petrov, Korshak and co-workers [3, 4 and 19] have reported the copolymerization of a series of allyl derivatives of silicon with methyl methacrylate and styrene.

We thought it would be of value to explore the likelihood of obtaining alkenylsilane copolymers with propylene in the presence of the complex catalyst $(C_2H_5)_3Al+TiCl_4$. This is of considerable importance both for extending our knowledge of the mechanism underlying stereospecific polymerization and also as regards changes in the properties of polyolefines. It is not unlikely that similar copolymers will differ from the polyolefines by high thermal stability and the ability to withstand low temperatures. The present communication describes the copolymerization of dimethyl and methylphenyldiallylsilanes with propylene in the liquid phase on the complex catalyst $(C_2H_5)_3Al+TiCl_4$.

The copolymerization experiments were conducted on the apparatus schematically represented in Fig. 1 at 65–70°C and a pressure of 30–40 atm and were terminated at 60–80 per cent conversion of the propylene. The starting monomers used were dimethyldiallylsilane (n_D^{20} 1·4445, d_4^{20} 0·7672), methylphenyldiallylsilane (n_D^{20} 1·5220, d_4^{20} 0·9090) and a propane-propylene fraction of the

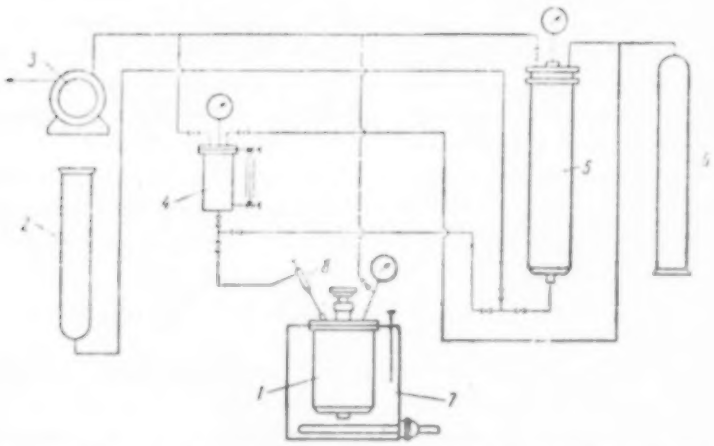

FIG. 1. Apparatus for the copolymerization of silicon diallyl derivatives with propylene in the liquid phase. (1) Autoclave, (2) Flask containing propane–propylene fraction, (3) Gas meter, (4) Measuring tank, (5) Desiccator, (6) Flask containing argon, (7) Autoclave heater, (8) Steel ampoule.

following composition: propane = 72 per cent, propylene = 26 per cent, ethane = 1·2 per cent and ethylene = 0·8 per cent.

From flask 2 the propane-propylene fraction was fed into the desiccator 5 filled with aluminium oxide from where (with a dew point not higher than −40°C) it was passed into the 1·5 l. measuring tank 4 fitted with a level gauge

and then under compressed dry nitrogen from 6 it was introduced via the steel ampoule 8 into the autoclave 1 which had been heated to the required temperature and was fitted with a stirrer (540 rev/min). With copolymerization of dimethyldiallylsilane and propylene the autoclave was charged on attainment of the given temperature with about 500 ml of the propane–propylene fraction and $TiCl_4$ dissolved in 10 ml absolute *n*-heptane, then triethyl aluminium and dimethyldiallylsilane were added one after the other in small amounts by displacement of the propane-propylene fraction.

In the experiments on the copolymerization of methylphenyldiallylsilane with propylene the autoclave was charged in sequence with methylphenyldiallylsilane, the propane-propylene fraction (about 1000 ml) and $TiCl_4$ dissolved in 10 ml absolute *n*-heptane. Triethyl aluminium was next added in small amounts. On completion of the experiments the reaction mass was treated with *iso*propyl alcohol at 70°C for 1 hr.

The polymers extracted from the autoclave were suction filtered on cloth filters then washed several times with *iso*propyl alcohol to a 0·05–0·1 per cent ash content. After drying at 70–80°C the copolymers were white, powdery substances. The atactic component of the copolymer was determined by extraction with boiling ethyl ether. The silicon content, intrinsic viscosity and melting point were determined of the starting copolymers and of the residues obtained after extraction with boiling ethyl ether. X-ray diagrams, thermograms and thermomechanical curves were recorded for a number of copolymer samples, and in addition their strength and specific elongation were also determined.

The influence of the ratios of the silicon allyl derivatives and propylene, triethyl aluminium and $TiCl_4$ on the yield and properties of the resulting poly.

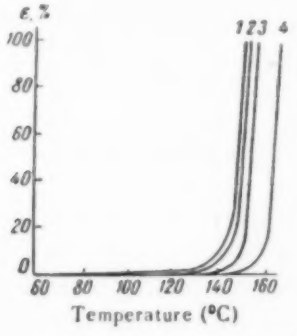

FIG. 2. Thermomechanical curves for copolymers of dimethyldiallylsilane (1, 2) and methylphenyldiallylsilane (3, 4) with propylene.

mers were examined. In studying the influence of the ratio of triethyl aluminium and $TiCl_4$ (K) on the copolymerization of dimethyldiallylsilane and methylphenyldiallylsilane with propylene the reaction was conducted with molar ratios

of triethyl aluminium and $TiCl_4$ of 1; 2; 3; 5 and 7 for dimethyldiallylsilane and 2 and 3 for methylphenyldiallylsilane. The total amount of catalyst was constant in all experiments, i.e. 11·25 g $(C_2H_5)_3Al+TiCl_4$), corresponding to 1·5 per cent of the propane-propylene fraction. The amount of silicon diallyl derivatives and the propane-propylene fraction introduced also remained constant: 30·7 g dimethyldiallylsilane, 40·0 g methylphenyldiallylsilane and 750 g of the propane–propylene fraction were reacted. The maximum copolymer yield was at molar ratios of the triethyl aluminium and $TiCl_4$ of 2 and 3. The amount of atactic material in the copolymers of dimethyldiallylsilane and methylphenyldiallylsilane with propylene is approximately constant (~52 per cent) at $K=2$, 3 and 5 and increases at $K=1$ and 7 (Table 1).

In all the experiments to study the influence on copolymerization of the ratio of the dimethyl and methylphenyldiallylsilane and propylene, 750 g were used. The ratio of the triethyl aluminium and the $TiCl_4$ was equal to 2. The total amount of the catalyst complex was 2·5 per cent of the sum of the unsaturated substances in the raw material introduced. The copolymers obtained on raising the molar ratio of silicon diallyl derivatives to propylene from 0·04 to 0·15 had a slightly higher softening point and gradually lost their complete solubility in decalin (even on heating to 150°C for 10–12 hr) (Table 2).

A comparison of the mechanical properties of both methylphenyldiallylsilane-propylene and dimethyldiallylsilane–propylene copolymers revealed that the latter have roughly half the tensile strength of the former. The copolymers of methylphenyldiallylsilane with propylene are characterized by a high specific elongation (600–700 per cent).

With an increasing relative amount of methylphenyldiallylsilane in copolymers with propylene their thermo-mechanical properties improve markedly (Fig. 2, curves 3, 4) relative to those of the dimethyldiallylsilane–propylene copolymers (Fig. 2, curves 1, 2).

CONCLUSIONS

(1) Silicon diallyl derivatives are shown to be capable of copolymerizing with propylene in the liquid phase on the complex catalyst $(C_2H_5)_3Al+TiCl_4$.

(2) The yield and physical-chemical properties of the copolymers are studied as a function of the molar ratios of: (a) triethyl aluminium and $TiCl_4$, (b) silicon diallyl derivatives and propylene. The maximum copolymer yields are attained for molar ratios of triethyl aluminium and $TiCl_4$ equal to 2 and 3. With an increasing molar ratio of silicon diallyl derivatives and propylene an improvement comes about in certain mechanical properties of the copolymers.

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TABLE 1. EFFECT OF TRIETHYL ALUMINIUM/$TiCl_4$ RATIO ON COPOLYMERIZATION OF DIMETHYL AND METHYLPHENYLDIALLYLSILANE WITH PROPYLENE ON THE COMPLEX CATALYST $(C_2H_5)_3$ Al+$TiCl_4$

Molar ratio $\frac{(C_2H_5)_3Al}{TiCl_4}$	Mols. $(C_2H_5)_3Al$	Mols. $TiCl_4$	Mols. $R_2Si(CH_2CH=CH_2)_2$	Molar ratio $\frac{R_2Si(CH_2CH=CH_2)_2}{C_3H_6}$	Copolymer before extraction with ether: Copolymer yield as % of unsaturated starting substance	Copolymer before extraction with ether: $[\eta]$	Copolymer before extraction with ether: M. pt. (°C)	Copolymer before extraction with ether: % content of Si	Copolymer after extraction with ether: % copolymer yield	Copolymer after extraction with ether: $[\eta]$	Copolymer after extraction with ether: M. pt. (°C)	Copolymer after extraction with ether: % content of Si
Dimethyldiallylsilane—propylene copolymer												
1	0·037	0·037	0·22	0·046	49·8	0·35	—	—	20·0	0·71	135–154	—
2	0·054	0·027	0·22	0·046	49·8	0·92	130–146	1·6	48·0	1·55	148–155	—
3	0·063	0·21	0·22	0·046	57·1	1·25	140–151	0·8	48·0	1·35	145–152	—
5	0·075	0·015	0·22	0·046	33·1	1·6	137–151	0·52	48·2	1·9	153–156	—
7	0·079	0·011	0·22	0·046	10·8	0·5	128–145	—	29·9	0·4	137–151	—
Methylphenyldiallylsilane—propylene copolymer												
2	0·0544	0·0266	0·198	0·0415	73·0	1·65	146–156	3·0	44·3	Insoluble	155–173	2·80
3	0·0630	0·0210	0·198	0·0415	42·5	1·25	151–164	1·20	43·3	1·7	150–171	1·25

TABLE 2. EFFECT OF SILICON DIALLYL DERIVATIVE/PROPYLENE RATIO ON COPOLYMERIZATION OF DIMETHYL AND METHYLPHENYLDIALLYLSILANE WITH PROPYLENE ON THE COMPLEX CATALYST $(C_2H_5)_3Al+TiCl_4$

Molar ratio $\frac{(C_2H_5)_3Al}{TiCl_4}$	Mols. $(C_2H_5)_3Al$	Mols. $TiCl_4$	Charge of $R_2Si(CH_2CH=CH_2)_2$ in mols	Molar ratio $\frac{R_2Si(CH_2CH=CH_2)_2}{C_3H_6}$	Copolymer before extraction with ether: Copolymer yield as % of unsaturated starting substance	Copolymer before extraction with ether: $[\eta]$	Copolymer before extraction with ether: M. pt (°C)	Copolymer before extraction with ether: % content of Si	Copolymer after extraction with ether: % copolymer yield	Copolymer after extraction with ether: $[\eta]$	Copolymer after extraction with ether: M. pt. (°C)	Copolymer after extraction with ether: % content of Si
Dimethyldiallylsilane–propylene copolymer												
2	0·054	0·027	0·220	0·046	49·8	0·92	130–146	1·6	48·0	1·55	148–155	—
2	0·101	0·051	0·714	0·149	51·5	Insoluble	148–160	3·5	42·8	Insoluble	150–165	3·65
Methylphenyldiallylsilane–propylene copolymer												
2	0·0544	0·0266	0·198	0·0415	73·0	1·65	151–164	3·0	44·3	Insoluble	155–173	2·80
2	0·0715	0·0360	0·495	0·103	47·3	1·25	144–158	—	34·0	1·85	157–178	—
2	0·0763	0·0381	0·717	0·150	59·2	Insoluble	140–155	6·3	27 7	Insoluble	155–175	3·1

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SYNTHESIS AND INVESTIGATION OF STEREO REGULAR COPOLYMERS OF PROPYLENE AND ISOPRENE*

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THREADS and films of stereoregular polypropylene possess a number of technically valuable properties but they have important shortcomings which limit their use in a number of crucial fields, in particular the production of high-strength cord. This shortcoming consists of the comparatively low softening temperature and, correspondingly, the noteworthy decrease in strength of polypropylene threads on raising the temperature. Thus, on raising the temperature to 80° the strength of a filament is reduced to 40 per cent and at 100° the filaments begin to flow. If one were to succeed in eliminating this shortcoming, the possibility of using high-strength elastic polypropylene filaments for the production of cord would become a reality.

One of the possible answers to this complicated and practically important problem is the formation of a small number of chemical bonds between the propylenemacromolecules. The formation of chemical bonds (vulcanization) to propylene may be carried out in various ways. One of the most interesting methods is the synthesis of polypropylene containing a small quantity of diene units (e.g. isoprene) with subsequent vulcanization at the position of the double bond in the copolymer obtained (as in the vulcanization of butylrubber). Starting from this postulate we synthesized copolymers of polypropylene and isoprene and carried out preliminary experiments on their vulcanization; the results obtained are set out in brief in this article.

Synthesis of copolymers of propylene and isoprene. The copolymerization of propylene with isoprene was carried out in an autoclave at 8–10 atm. in the presence of catalysts based on organoaluminium compounds and titanium chloride according to two methods previously described by us [2]. Dry, thoroughly purified *n*-heptane was used as solvent. The catalyst concentration in the heptane solution was 4 per cent by weight. The catalysts used for the copolymerization were $Al(C_2H_5)_3+TiCl_4$ and $Al(C_2H_5)_3+TiCl_3$. The conditions and results of these experiments are put in Table 1.

* Vysokomol. soedin. **1**: No. 12, 1758–1763, 1959.

At the end of the copolymerization the reaction mixture was reacted with absolute *iso*propanol to destroy the residual catalyst and the copolymer obtained was dried to constant weight in vacuum at 50–60°. For example, the following were determined: the degree of unsaturation, the specific viscosity in decalin at 120°, the melting temperature and the yield of copolymer. At the same time the amount of amorphous fraction was determined by dissolving it in toluene at 20°; in order to compare the generality of the method, the solubility of the copolymer in ether and heptane was determined. An increase in the concentration of isoprene noticeably lowered the yield of copolymer in the reaction with the catalyst $Al(C_2H_5)_3+TiCl_4$; at the same time the content of amorphous fraction, soluble in ether, increased.

TABLE 1. PREPARATIVE CONDITIONS AND PROPERTIES OF PROPYLENE/ISOPRENE COPOLYMER

Concentration of isoprene (wt. %)	Polymer obtained (g)	specfiic viscosity [η]	M.p. (°C)	Solubility (wt %)		Content of isotactic copolymer
				in ether	in pentone	
System $Al(C_2H_5)_3+TiCl_4$: molar ratio of $Al(C_2H_5)_3$: $TiCl_4=3:1$; experimental temperature						
0	148	1·80	157–162	30·0	25·0	45·0
1·0	133	1·60	155–158	34·0	26·0	40·0
2·5	103	1·50	150–156	33·0	29·0	38·0
5·0	30	1·30	148–157	41·0	31·0	28·0
7·5	22	1·58	142–149	60·0	25·5	14·5
10·0	20	1·60	150–156	56·0	32·0	12·0
System $Al(C_2H_5)_3+TiCl_3$: molar ratio of $Al(C_2H_5)_3$: $TiCl_3=1:1$; temperature of the experiment						
0	210	1·80	156–160	13·0	41·0	46·0
2·5	190	1·80	154–160	15·0	59·0	36·0
5·0	190	1·50	154–163	15·5	52·5	32·0
7·5	195	2·00	143–150	16·0	27·0	57·0

The number of diene groups in the copolymer obtained was estimated by the number of double bonds. The unsaturation was determined by reaction with the Interhalogen ICl which added to the copolymer at the double bond. This method is generally used for butyl-rubber containing 1–5 per cent of diene (butadiene or isoprene). The data obtained, which is displayed in Table 2, shows that the number of double bonds in the copolymer increases regularly with the increase in quantity of isoprene used in the copolymerization reaction.

The distribution of the isoprene residues between the crystalline and amorphous fractions of the polypropylene was unequal. The main quantity of isoprene, characterized by the presence of double bonds (degree of unsaturation),

TABLE 2. INFLUENCE OF THE QUANTITY OF ISOPRENE USED IN THE POLYMERIZATION ON THE UNSATURATION OF THE COPOLYMER OBTAINED

Concentration of isoprene in pentone solution	Unsaturation of the copolymer (wt.%)	
	I	II
1·0	0·375	—
2·5	0·455	0·510
5·0	0·974	1·260
7·5	—	1·840
10·0	1·33–1·54	—

Note. Copolymer I was obtained with the catalyst $Al(C_2H_5)_3 + TiCl_4$; Copolymer II with the catalyst $Al(C_2H_5)_3 + TiCl_3$.

is found in the amorphous fraction (Table 3). Such a distribution is quite understandable because with an increase in the isoprene content of the copolymer molecule the regularity of its structure decreases; correspondingly the crystallinity of the sample decreases and its solubility in toluene increases.

Investigation of the possibility of vulcanizing the propylene/isoprene copolymer. Samples of the copolymer with a degree of unsaturation of 1·33–1·8 per cent were taken for investigating the possibility of vulcanization i.e. a sample with

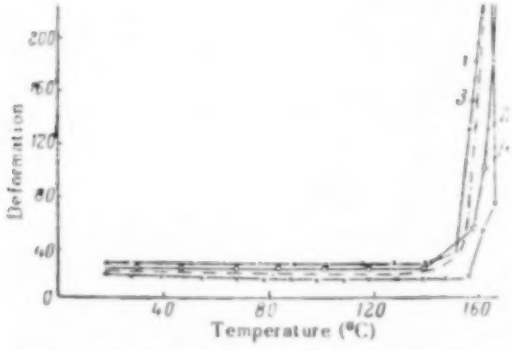

FIG. 1. Thermochemical properties: (1) polypropylene, (2) copolymer with 1%, (3) copolymer with 5%, (4) with 10% of isoprene.

the same unsaturation as preparations of butyl-rubber which was a degree of unsaturation of 1·4–1·5 per cent. Methods used for vulcanizing various types of rubber, in particular butyl rubber, were used for vulcanizing the copolymer.

(a) *Vulcanization with sulphur in the presence of accelerators* (using the method as for vulcanizing butyl rubber).

TABLE 3. THE DEGREE OF UNSATURATION OF CRYSTALLINE AND AMORPHOUS FRACTIONS OF THE PROPYLENE/ISOPRENE COPOLYMER

Description of the preparation	Conc. of isoprene in heptane sol. (wt. %)	Qtty. of product, % wt. of the copolymer	Unsaturation (%)	Application
1. Unfractionated copolymer	5	100	0·974	Polymerization was carried out in the presence of the catalyst $Al(C_2H_5)_3 + TiCl_4$
(a) crystalline fraction	—	62·4	0·124	
(b) amorphous fraction	—	29·82	2·11	
2. Unfractionated copolymer	10	100	1·34–1·54	
(a) crystalline fraction	—	68·6	0·28–0·37	The same
(b) amorphous fraction	—	26·6	4·2–4·75	
3. Unfractionated copolymer	2·5	100	0·506	Polymerization was carried out in the presence of the catalyst $Al(C_2H_5)_3 + TiCl_3$
(a) crystalline fraction	—	87·4	0·0	
(b) amorphous fraction	—	10·2	1·3	
4. Unfractionated copolymer	7·5	100	1·81	
(a) crystalline fraction	—	87·2	0·422	The same
(b) amorphous fraction	—	11·0	6·05	

Note. The fractionation was carried out by fractional solution in toluene at 20°. In these conditions the amorphous fraction is dissolved [3]. The introduction of a larger or smaller number of isoprene groups into the macromolecule copolymer (by adding to the copolymerization from 1 to 10 per cent of isoprene) does not influence the character of the thermomechanical curves of these copolymers and, consequently, the change in fluidity of the copolymer.

Composition of the vulcanizing mixture (in g per 100 g of polymer): sulphur—2·0, thiuram—1·3, "kaptaks"—0·65, zinc oxide—5·0, stearin—3·0; vulcanization temperature 100–145°; duration 30–120 min. Vulcanization was carried out in a press.

Because stereoregular polypropylene has little stability to oxidative destruction at high temperature, then, to eliminate the side effects of the process of oxidative destruction, mixtures of the copolymer with the vulcanization

reagents were mixed in a rolling mill, and heating of the mixture was carried out in parallel in air and under vacuum in sealed tubes from which the air had been previously removed down to a pressure of 10^{-6} mm.

(b) *The ultrafast vulcanization method* by reacting the copolymer with sulphur monochloride (either as gaseous S_2Cl_2 or as a 5% solution of S_2Cl_2 in benzene). Length of reaction 15–60 min, temperature 20°.

Treatment with the benzene solution of sulphur monochloride ensures some swelling of the copolymer and thus increases the possibility of diffusion of the vulcanization reagent into the polymer.

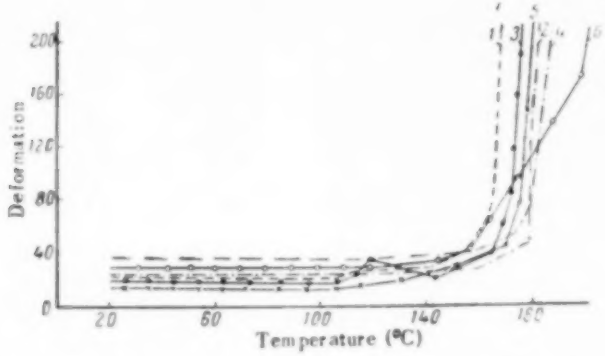

FIG. 2. Thermochemical properties of the copolymer after vulcanization: (1) copolymer heated to 100° for GL., (2) to 150° for 2 hr, (3) copolymer heated to 150° for 2 hr, (4) at 100° for 6 hr, in nitrogen, (5) copolymer heated to 150° for 2 hr, (6) to 100° for 6 hr, in vacuum.

The following estimations were carried out to determine the amount of chemical bonding between the copolymer molecules resulting from the treatment described: (a) the quantity of combined sulphur after vulcanization; (b) the change in the degree of unsaturation of the copolymer; (c) the change in the character of the thermomechanical curves of the copolymer before and after vulcanization.

The quantity of combined sulphur in the sample after vulcanization was determined by the method adopted in the resin industry—the free sulphur is extracted with acetone from the sample submitted to vulcanization and subsequently the quantity of combined (non-extractable) sulphur is determined by normal methods. However, control experiments showed that it was impossible to remove free sulphur from thick rolled samples of the copolymer or polypropylene. Thus, for example, polypropylene, rolled with a sulphur preparation and then extracted with acetone for 26–36 hr, contained 0·9 per cent combined sulphur. *Cyclo*hexane was used in place of acetone to increase the extraction temperature; but this solvent did not permit the complete removal of sulphur

from polypropylene. Therefore one cannot use the determination of the quantity of combined sulphur as a characteristic of the number of chemical bonds formed between the macromolecules.

The change in properties of the polymer as a result of the formation of chemical bonds between the macromolecules is demonstrated by the character of the thermomechanical curve (the change in fluidity of the material on increasing the temperature) which is determined by various methods, in particular by Kargin's balance. When chemical bonds between the macromolecules appear the fluidity of the material should fall sharply, but in the presence of a large number of bonds, the polymer in general should not flow on increasing the temperature. The character of the thermomechanical curve should also change sharply. Trials showed that chemical bonds between the copolymer macromolecules were not formed on vulcanization under the conditions described above. As is evident from Fig. 2, the thermomechanical curves of the copolymer did not change after rolling with a vulcanization mixture and after heating either in air or in vacuum for various times and various temperatures. There was no change in the degree of unsaturation either.

It is obvious that chemical bonds were not formed between the macromolecules in the vulcanization conditions described; negative results were obtained with both variants of sulphur monochloride vulcanization.

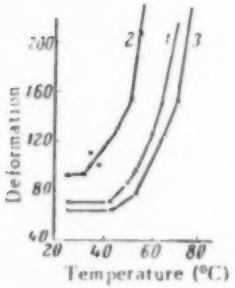

FIG. 3. Thermochemical properties: (1) initial fraction, (2) amorphous fraction of the copolymer, vulcanized in air, (3) same in vacuum.

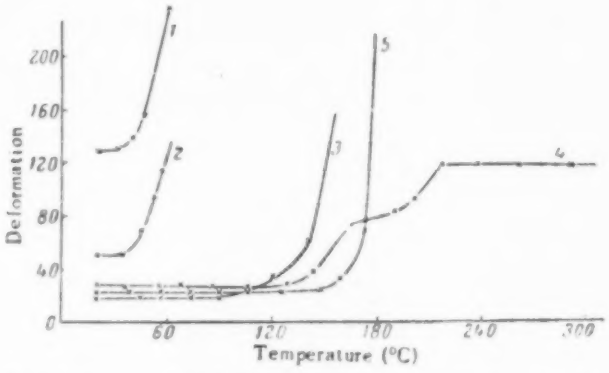

FIG. 4. Thermochemical properties before and after irradiation: (1) amorphous fraction irradiated with γ-rays (50 million roentgen), (2) the same, not irradiated, (3) unfractionated specimen SPI-12, irradiated in air (150 million roentgen), (4) the same in vacuum (150 million roentgen), (5) the same sample, not irradiated.

To elucidate the possibility of vulcanization of the propylene/isoprene copolymer with sulphur, the vulcanization was carried out with the amorphous fraction of the copolymer which had the highest degree of unsaturation (6·11 per cent). This fraction was mixed with a vulcanizing mixture in the rolling mill

and submitted to heating under the same conditions; but as is evident from Fig. 3, the character of the thermomechanical curve for this fraction also did not change after vulcanization. Therefore, we attempted to use physical methods, especially irradiation with γ-rays, instead of chemical methods, for forming chemical bonds between the macromolecules of the copolymer.

The stereoregular copolymer of propylene and isoprene synthesized by us was irradiated with γ-rays of varying intensity.* A radiation dose of 15 to 150 million roentgen was used, either in air or in high vacuum. The change in the number of double bonds and in the molecular weight (by viscometric measurements) were determined for the irradiated samples, and thermomechanical curves were constructed. The results obtained are put in Table 4 and Fig. 4.

As can be seen from these data, a considerable destruction of the copolymer takes place when it is irradiated at various intensities in air, and this leads to a lowering of the initial temperature of flow of the material after irradiation. Chemical bonds between the macromolecules are not formed in these conditions of treatment and consequently the character of the thermomechanical curves of these preparations is not changed. Formation of chemical bonds between the macromolecules is observed or irradiation in vacuum with the maximum dose used by us—150 million roentgen—and this is confirmed by the sharp change in the thermomechanical curve of this preparation. The data in Fig. 4 show that this preparation does not soften at the temperature at which the initial sample of polypropylene begins to flow (160°) and this material does

TABLE 4. CHANGES IN THE DEGREE OF UNSATURATION AND THE VALUE OF THE SPECIFIC VISCOSITY FOR PREPARATIONS OF THE COPOLYMER OF PROPYLENE AND ISOPRENE AFTER IRRADIATION

Condition of irradiation		Properties of the preparation			
Dose (min) r	Character of the medium	Degree of unsaturation (%)		Spec. viscosity of a 0·125% solution	
		before irradiation	after irradiation	before irradiation	after irradiation
15	Air	1·8	0·47	0·4	0·07
15	Vacuum	1·8	0·98	0·4	0·37
50	Air	1·8	0·54	0·4	0·07
50	Vacuum	1·8	0·97	0·4	insoluble
150	Air	1·8	0·71	0·4	0·014
150	Vacuum	1·8	0·95	0·4	insoluble

Note. A copolymer of propylene with 7·5% isoprene, made with the catalyst $Al(C_2H_5)_3 + TiCl_3$, was used for the irradiation.

* The irradiation was carried out at the Karpov Physico-chemical institute by Iu. M. Malinskii, to whom we convey our thanks.

not melt at much higher temperatures even up to 280°. Evidently under these conditions vulcanization of the stereoregular copolymer of propylene and isoprene can be carried out.

SUMMARY

(1) Stereoregular copolymers of the propylene with isoprene containing a small number of diene groups have been synthesized.

(2) The possibility of vulcanizing the copolymers obtained has been investigated. It has been shown that the formation of chemical bonds between the macromolecules does not place when chemical methods of vulcanization are used.

(3) Vulcanization of the stereoregular copolymer of propylene and isoprene can only be carried out by irradiation with high intensity rays in vacuum.

Translated by M. J. NEWLANDS

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STUDIES IN CO-ORDINATION-CHAIN POLYMERS—I. PREPARATION OF POLYMERS OF *BIS*(β-DIKETONES) WITH METALS*

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IN most high molecular compounds which are known at the present time the basic chain of the macromolecule is built with covalent bonds. Only recently it has been shown possible to build polymer chains containing atoms of various metals joined by coordinate bonds [1–5]. It is possible to obtain polymers containing co-ordinate-bonded metal atoms in the following ways.

(1) Starting from polymers which contain functional groups capable of complexing with metal ions.

(2) Polymerization or polycondensation of certain complex compounds which have functional groups which permit these reactions.

(3) By obtaining polymers in which the co-ordinate-bonded metal ions cause the formation of the polymer itself, being included in the basic chain of the polymer (polyco-ordination).

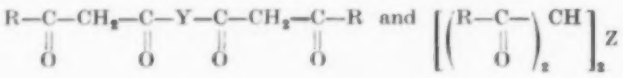
Martin [2] showed that it was necessary to have the molecular structure I to obtain a linear polymer of the last type:

X and Y are donor atoms; two of these donor atoms must be linked to a hydrogen atom possessed of protonic mobility. When it is reacted with a divalent metal of co-ordination (4) (Cu^{2+}, Ni^{2+}, Zn^{2+} etc.,) each molecule of I loses two protons and a linear polymer is formed (II).

Several examples of this type of reaction have been described. Wilkins and Wittebecker [3] treated a series of tetraketones with beryllium salts and obtained polymers which had structures similar to II. Co-ordination polymers were obtained from 4-hydroxy-5-phenylsalicabdehyde (5), *bis*-α-thiopicolamide [2] and others.

* Vysokomol. soedin. 1: No. 12, 1764–1771, 1959.

In the present article the preparation of a series of co-ordination polymers based on *bis*-β-diketones of two types is described:



We have synthesized the following tetraketones: adipyldiacetophenone, 1,1,3,3-tetraacetylpropane, 4,4′-*bis*-(acetoacetyl)-diphenylmethane, *tere*phthalyldiacetone and *tere*phthalyldiacetone. *Tere*phthalyldiacetophenone was obtained by the condensation of dimethyl*tere*phthalate with acetophenone in the presence of sodamide by the method described [6] but with some modifications. *Tere*phthalyldiacetone was prepared by the interaction of *p*-diacetylbenzene with acetic anhydride in the presence of boron trifluoride. 4,4′-*bis*-(acetoacetyl)-diphenylmethane was made by condensing 4,4′-diacetyldiphenylmethane with ethyl acetate in the presence of metallic sodium.

Tetraketone of the second type $[(RCO)_2CH]_2Z$ was obtained by the interaction of sodium acetylacetonate and α-,ω-dibromoalkanes. Tetraacetylpropane was made by the condensation of formaldehyde with acetylacetone in the presence of diethylamine [7].

Divalent metals with co-ordination four (copper, nickel, beryllium, zinc, cobalt, etc.) were taken for reaction with the tetraketones.

The preparation of the *bis*-(β-diketone) co-ordination-chain polymers was carried out in two ways: the interaction of aqueous solutions of the acetates of the respective metals with alcoholic solutions of the *bis*-(β-diketones), or heating the stoichiometric quantity of the acetylacetonate of the corresponding metal with the tetraketone in vacuum, sometimes in a high-boiling solvent. In the latter case acetylacetone is eliminated and the metallic derivative of the initial tetraketone is formed.

The derivatives of the $[RCOCH_2CO]_2Y$ type tetraketones (*tere*phthalyldiacetophenone, *tere*phthalyldiacetone and 4,4′-*bis*-(acetoacetyl)-diphenylmethane with ions of the metals Cu, Ni, Co, Zn, Cd etc. were obtained in the form of coloured powders, slightly soluble or insoluble in the usual organic solvents. The specific viscosity in dimethylformamide was determined for the soluble products.

The elementary analysis of these compounds is equivalent to the elements contained in the polymer formula with the following structure:

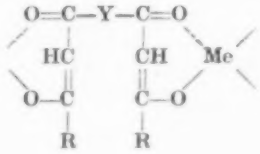


TABLE 1. PROPERTIES OF PRODUCTS FROM *bis*-β-DIKETONES AND VARIOUS METALS

bis-β-Diketones	Metal	Colour	Temperature of decomposition (°C)	Solubility in organic solvents
Adipyldiacetophenone	Cd	Light-green	132–140	Poorly soluble in dimethylformamide
	Co	Yellow	182–206	
	Cu	Green	230–260	
	Mn	Rose	160–170	
Tetra acetylpropane	Zn*	Yellow	195–200	Soluble in dimethylformamide, chloroform and methanol
	Co*	Green	230–240	
	Cu	Light-green	240–250	
4,4′-*bis*-(Acetonacetyl)-diphenylmethane)	Cd*	Yellow	118–120	Soluble in dimethyl formamide only
	Mn*	Rose	240–250	
	Zn*	Yellow	200–210	
	Co*	Yellow	260–270	
	Ni	Light-green	240–250	
	Cu*	Green	295–300	
	Cu	Green	280–285	
*Tere*phthalyldiacetone	Cu	Green	340–350	Not soluble
	Be	Light-yellow	400	
*Tere*phthalyldiaceto-phenone	Cd*	Yellow	295–300	The same
	Mn*	Rose	240–250	
	Zn*	Yellow	300–310	
	Co*	Yellowish-red	350	
	Cu*	Deep-yellow	370	
	Cu	The same	400	
	Hg*	White	400	

* Metal acetates used; in the other cases the metal acetylacetonates were used.

where

(a) $R = C_6H_5$, CH_2; $Y = p\text{-}C_6H_4$,

(b) $R = CH_2$, $Y = -C_6H_4-CH_2-C_6H_4-$

Me = Cu, Ni, Zn, Co, Hg, Mn, Cd, Be.

The melting points of the polymers obtained lay above 200°, except for the cadmium polymers which melted ~140°.

In Tables 1 and 2 are collected some characteristics of the prepared coordination compounds.

TABLE 2. CHARACTERISTICS OF PRODUCTS FROM *bis*-(β-DIKETONES) AND VARIOUS METALS

bis-(β-Diketone)	Metal	Elementary composition (%)						Coefficient of polymerization
		carbon		hydrogen		metal		
		required	found	required	found	required	found	
Adipyldiacetophenone	Cd	57·39	63·17	4·75	5·63	24·52	13·73	1
	Co	64·81	62·95	4·93	4·84	14·5	18·88	—
	Cu	64·54	64·08	4·83	4·72	15·43	15·54	∞
	Mn	65·49	62·65	5·48	5·53	13·64	12·52	9
Tetraacetylpropane	Zn*	47·10	48·54	5·10	4·73	23·6	23·19	∞
	Co*	49·3	50·36	5·22	5·36	21·9	19·8	7
	Cu	48·3	47·16	5·15	5·65	23·2	21·81	11
4,4′-*bis*-(Acetoacetyl)-diphenylmethane	Cd*	55·0	62·15	4·21	4·97	19·65	13·49	1
	Mn*	64·5	63·37	5·12	4·87	14·1	14·61	∞
	Zn*	62·4	61·16	5·46	5·49	16·2	15·15	10
	Co*	63·7	59·14	5·05	5·09	15·0	17·52	—
	Ni	64·12	62·52	5·09	5·25	15·0	11·5	3
	Cu*	63·4	60·64	4·52	4·53	16·08	16·37	∞
	Cu	63·4	63·91	4·52	4·69	16·08	16·03	∞
*Tere*phthalyldiacetone	Cu	54.66	51·28	3·90	4·05	20·68	24·92	—
	Be	66·44	66·47	4·74	4·71	3·56	3·33	∞
*Tere*phthalyldiacetophenone	Cd*	61·91	56·98	3·73	3·97	23·23	21·56	∞
	Mn*	67·81	65·18	4·29	4·74	12·95	9·05	—
	Zn*	66·01	61·04	4·13	4·43	15·0	13·21	—
	Co*	67·34	67·15	4·2	4·97	13·9	14·33	∞
	Cu*	66·48	64·25	4·15	3·84	14·72	15·91	—
	Cu	66·48	66·21	4·15	3·92	14·7	13·39	—
	Hg*	50·07	50·61	3·16	2·91	35·12	35·32	∞
	Be*	76·01	74·02	4·75	4·47	2·37	2·75	—

* Metal acetates were used; in the rest of the cases metal acetyl-acetonates were employed.

DISCUSSION OF RESULTS

It is still very difficult on the basis of presently-available experimental evidence to draw comprehensive conclusions about the dependence of the properties of the polymetallic derivatives on the structure of the *bis*-β-diketones and on the type of metal. However, some measure of all this becomes evident from an analysis of the data in the literature about the properties of certain metallic derivatives of β-diketones and comparison of these data with those obtained in the present investigation.

Thus Van Wistert, Fernelius and Duglas [7] compiled the following empirical stability series for complex derivatives of various β-diketones with divalent tetraco-ordinated metals (in order of decreasing stability):

TABLE 'A'

Metal	Hg	Cu	Be	Fe	Ni	Co	Zn	Pb	Mn	Cd	Mg	Ca	Sr	Ba
pK	—	15·16	14·63	—	10·77	9·57	9·02	—	7·35	6·72	6·38	—	—	—

On comparing this series with the acetylacetonate (8) instability constants ($pK = -\log K$) shown it is evident the series of decreasing stability depends on the nature of the metal. This circumstance rightly permits us to compare the thermal stability of the polymetallic derivatives of tetraketones obtained by us, with the instability constants of the acetylacetonates shown above.

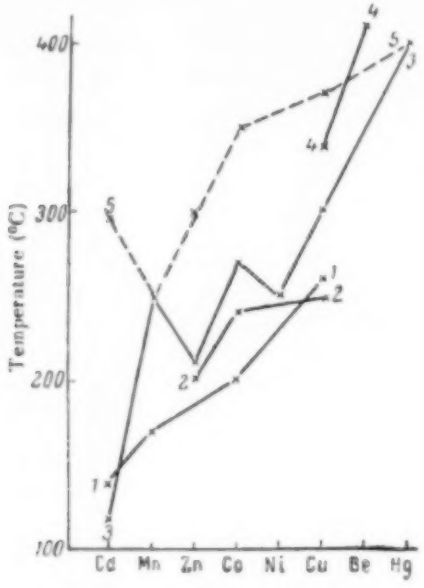
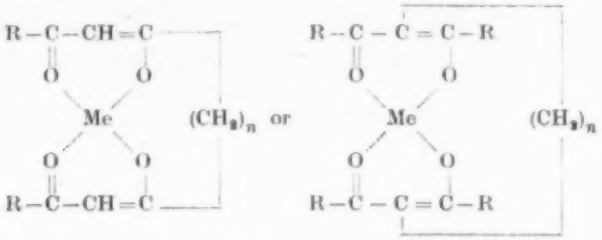


FIG. 1

In Fig. 1 the metals from which we made tetraketone derivatives are placed on the abscissa in order of increasing stability of their acetylacetonates. On the ordinate is placed the value of the thermal stability of the derivatives prepared from the tetraketones. It is evident from the graphs shown that these generally show the regularity which characterised Van Wittert and Fernelius' series; this is an extraordinarily important effect on the basis of which it is possible to give an estimate beforehand of the thermal stability of a polymetallic derivative by comparing it with the known instability constant of the same type of compound. The divergences from this regularity may be explained by differences in the molecular weights of the polymetallic derivatives of the tetra-

ketones, which is possibly linked with changes in the spacial configuration of the polyco-ordination compounds depending on the ionic radius of the metal; evidently a sufficiently flexible chain and closely spaced carbonyl groups permits (in some cases) the closing of a ring on one metal atom if its ionic radius does not prevent the formation of a ring of this type:



It should be noted that the thermal stability of polyco-ordination compounds based on *bis*-β-diketones having phenyl groups in the molecule do depend on the latter quality. Thus the greatest thermal stability of the derivatives investigated is possessed by *tere*phthalyldiacetophenone (three phenyl groups separated by three C-atoms) and the least—adipyldiacetophenone (two phenyl groups separated by ten C-atoms).

The most important characteristic of the derivatives made is the molecular weight. Unfortunately only the metallic derivatives of tetraacetylpropane were soluble in methanol, benzene, chloroform, tetrahydrofuran, dichloroethane, dimethylformamide and other solvents. Since the specific viscosity of the solutions of these compounds was small it can be assumed that the derivatives obtained were low-molecular. The metallic derivatives of all the other *bis*-β-diketones investigated were completely insoluble in the organic solvents named (above). An estimate of the molecular weights of some derivatives was carried out by the end group method.

Three variants of the polymer end group are possible in the formation of metallic derivatives of *bis*-β-diketones

(a) TK-Me-TK-Me . . . TK-Me-TK

(b) Acac-Me-TK-Me . . . TK-Me-TK

(c) Acac-Me-TK-Me . . . TK-Me-Acac

where TK—substituted tetraketone, Acac—substituted acetylacetone.

The molecular weight of the polymer, assuming that both end groups are tetraketone groups (variant a) may be expressed:

$$(M_{TK}-2+M_{Me})n+M_{TK}-1=M_p$$

where M_{TK}—molecular weight of tetraketone; M_{Me}—atomic weight of metal; M_p—mol. wt. of polymer; 2—mol.wt. of H_2; 1=mol. wt. of $H_2/2$; n=coefficient of polymerization.

If we designate the quantity of metal found in the derivative as Me%, then

$$\frac{M_{Me}\% \cdot n \cdot 100}{(M_{TK} - 2 + M_{Me})n + M_{TK} - 1} = Me\%,$$

whence it is possible to evaluate the coefficient of polymerization n and the mol. wt. of the polymer M_p.

The molecular weights of some of the metal derivatives were determined with the formula and showed the following values (Table 3).

TABLE 3. MOLECULAR WEIGHT OF SOME OF THE POLYMERS MADE

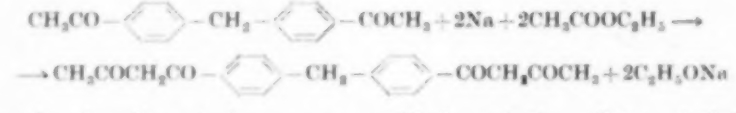
bis-β-Diketone	Adipyl-acetophenone		Tetracetyl-propane			4,4'-*bis* (Acetoacetyl) diphenyl-methane	
Metal	Cd	Mn	Co	Cu	Cd	Zn	Ni
n	7	9	7	11	1	10	3
M_p	811	4000	2200	3200	783	4300	1500

If it is considered that the values of the molecular weights cited in some degree reflect the real index, then it can be concluded that the polymers obtained are products with equally molecular weights.

EXPERIMENTAL SECTION

4,4-*Diacetyldiphenylmethane*. (a) 4,4'-bis-*acetoacetyl*)-*diphenylmethane*. To a vigorously stirred mixture of 80 g diphenylmethane, 200 g acetyl chloride and 400 ml of freshly distilled dichloroethane at 0–3°, 408 g of anhydrous $AlCl_3$ was added during $2^1/_2$ hr. Two hours after the completion of the addition of the $AlCl_3$ the reaction mass was poured into an ice/hydrochloric acid mixture. 4,4-'Diacetyldiphenylmethane was extracted with benzene, the benzene extract dried and, after distilling off the benzene, the residue was distilled in vacuum. 76 g of 4,4'-diacetyldiphenylmethane was obtained, a yield of 60 per cent, m.p. 92–93°, literature m.p. 93° [9].

(b) *Condensation of* 4,4'-*diacetyldiphenylmethane with ethyl acetate in the presence of powdered sodium*.



To powdered sodium in benzene was added a solution of 46 g 4,4'-diacetyldiphenylmethane in 200 ml ethyl acetate at 45–50°. After the addition it was heated for 3 hr and left overnight. Then the reaction mass was poured into water acidified with conc. hydrochloric acid and the precipitate formed was fil-

tered off. 16·5 g of the tetraketone was obtained; yield 27 per cent. After two recrystallizations from acetone m.p. was 136°.

Found %: C 75·03; 75·26; H 6·09; 6·18.

$C_{12}H_{20}O_4$. Required %: C 75·0; H 5·9.

Tere*phthalyldiacetophenone*. To a vigorously stirred mixture of 23·5 g of sodamide and 36 g of acetophenone in 300 ml absolute ether at 0–3°, 30 g of dimethyl *tere*phthalate was added in portions. The reaction mixture was stirred for a further 2 hr at room temperature and left overnight. Then the products of reaction were poured into an ice/water mixture and filtered from the considerable volume of precipitate formed. The filtrate was saturated with CO_2, when the required product precipitated out. Yield 3·0–5 per cent. After three recrystallizations from methanol m.p. 175–178°; literature m.p. 176–177° [6];

Found%: C 77·94; 77·73; H 5·17; 4·91.

$C_{24}H_{18}O_4$. Required %: C 77·82; H 4·86

Tere*phthalyldiacetone*. In a three-necked flask equipped with a stirrer, reflux condenser and a gas inlet tube, 16 g *p*-diacetylbenzene, 40 ml acetic anhydride and 180 ml of dichloroethane were mixed. The mixture was saturated with boron trifluoride during 2·5 hr while it was vigorously stirred and the reaction flask was cooled with a mixture of dry ice and chloroform. Then BF_3 was passed in for a further hour while the reaction mixture was heated to 80°. The precipitate was filtered off, dissolved in caustic soda and again filtered from foreign matter. The tetraketone was precipitated from the alkaline solution by acidifying with acetic acid to give a weakly acid reaction. After recrystallization from boiling alcohol, 8 g of yellow crystals with m.p. 187–188° were obtained; yield 35 per cent. Literature m.p. 186° [10].

Found %: C 68·22, 68·71; H 5·71; 5·89.

$C_{14}H_{14}O_4$. Required %: C 68·24; H 5·73.

Tetraacetylpropane. To a stirred mixture of 100 g acetylacetone and 15 g of *para*formaldehyde were added 40 drops of diethylamine. The mixture was heated to 65–70° until it was no longer homogeneous, and then it was allowed to stand for several days. The precipitate which had separated was filtered off, washed with ether and crystallized from alcohol. 21·4 g of the substance was obtained with a melting point of 79–82°; yield 21 per cent. The literature m.p. was 87–88° [11]. Found %: C 63·00; 62·97; H 7·53; 7·58

$C_{11}H_{16}O_4$. Required %: C 62·26; H 7·55.

Adipylacetophenone. To a stirred suspension of 25 g of sodamide in 350 ml absolute ether a solution of 80 g acetophenone in ether was added dropwise; after 2 hr 70 g of diethyl adipate was added at 0–5°. The reaction mixture was left overnight and afterwards decomposed with ice and water. The aqueous layer was removed and saturated with CO_2. 3 g of precipitate separated, which had a m.p. of 112–113° after recrystallization from methanol. The m.p. given in the literature [6] is 117°. Yield, 3 per cent of theory based on the amount of diethyl adipate taken.

Found %: 76·20; 75·98; H 6·38; 6·47

$C_{22}H_{22}O_4$. Required %: C 75·45; H 6·29.

Copper acetylacetone. To a boiling, continuously stirred mixture of 200 ml benzene and 100 ml acetylacetone 30 g of copper oxide was added in small portions, and the reaction mixture was allowed to boil for another 2 hr. The abundant precipitate formed was filtered off hot. After recrystallization from chloroform a blue coloure was obtained.

Nickel acetylacetonate [12]. To a stirred solution of 59·4 g of $NiCl_2.6H_20$ in water, a solution of 50 g of acetylacetone in 100 ml of methanol was added. To the mixture thus formed, a solution of 41 g sodium acetate was added and the whole heated rapidly. Then it was cooled to room temperature and stirred in the cold for several hours. The precipitate was filtered off, washed with water and crystallized from methanol. Green crystals were obtained, m.p. 136–140°, which were nickel acetylacetonate monohydrate.

Cobalt and beryllium acetylacetonates were prepared in a similar way to that of nickel.

Zinc acetylacetonate was prepared in the same way as copper acetylacetonate. Yellow crystals, m.p. 126–127°, were obtained after filtering and recrystallising.

Preparation of polymers from bis-(*β-diketones*). The polymetallic derivatives were obtained in two ways:

(1) By heating a stoichiometric mixture of the requisite metal acetylacetonate and tetraketone in vacuum at 200–250° until the evolution of acetylacetone ceased. In each case the theoretical quantity of acetylacetone was collected in the receiver; the polymer stayed in the reaction vessel and was obtained as a coloured powder (see Table 1).

(2) To an alcoholic solution of the *bis*-(*β*-diketone) an equimolecular quantity of a solution of the acetate of the requisite metal. The precipitate formed was filtered off and washed with alcohol (see Table 1). Only the metal derivatives of aromatic *bis*-(*β*-diketones) were obtained in this way. The metal derivatives of tetraacetylacetone were obtained in the following way: equimolecular quantities of dimethylformamide solutions of the tetraketone and the requisite metal acetate were mixed. In this way a change in the colour of the solution was observed but no precipitate formed. Then the solvent was evaporated in vacuum, maintained at 100° with a water bath, after which it was heated in vacuum (5 mm) at 200–220° until liquid ceased to come off. The solid residue was dissolved in dimethylformamide and precipitated from solution with alcohol or water.

SUMMARY

A series of *bis*-(*β*-diketones) of two types, $(RCOCH_2CO)_2Y$ and $[(RCO)_2CH]_2Z$ have been synthesized and from them polymetallic derivatives of some divalent tetraco-ordinated metals have been made.

Translated by M. J. NEWLANDS

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HETEROCHAIN POLYAMIDES—XXII. THE INFLUENCE OF SOME FACTORS ON THE FORMATION OF THE POLYAMIDE IN A TWO-PHASE SYSTEM*

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RESULTS OBTAINED

IN a previous paper [1] we demonstrated some of the merits of carrying out the formation of polyamides at the interface between two immiscible liquids compared with the normal manner of forming polyamides by polycondensation in the molten state. The basic merit consists in the non-equilibrium nature of the first reaction.

The aim of the present work was the investigation of the influence of a series of factors (duration and intensity of stirring, concentration of starting materials, reaction temperature, nature of the solvents and media for absorbing the acid formed during the reaction) on the molecular weight and yield of the polyamides in the non-equilibrium polycondensation reaction. In the non-equilibrium polycondensation reaction of dicarboxylic acid chlorides with diamides at the interface of two immiscible solvents, a film of polyamide is formed instantaneously.

We investigated the polycondensation of hexamethylenediamine (dissolved in water containing the calculated quantity of caustic soda to absorb the acid formed in the polycondensation), and adipyl chloride (dissolved in a solvent immiscible with water). The molar ratio of the reactants was kept at 1:1 and the reaction temperature at ~22°.

In Fig. 1 and 2 is shown the relation of the change in molecular weight and yield of the polyamide to the concentration of starting materials. Experiments were carried out both with stirring of the initial solutions (at stirring speed of ~7500 rev/min) and without stirring. In the first case the polymer was obtained in the form of separate lumps whereas in the second it was obtained in the form of a continuous film. Benzene, carbon tetrachloride and chloroform were used as solvents for the acid chloride.

In the investigation both starting reagents (hexamethylenediamine and adipyl chloride) were used in the form of solutions of equal molar concentrations. In all cases, as shown in Fig. 1, the greatest molecular weight was obtained by using

* Vysokomol. soedin. 1: No. 12, 1795–1800, 1959.

dilute solutions in which the concentration of the starting materials was kept at ~0·15 mole/l. When the reaction was carried out without stirring the starting materials the highest molecular weight of polymer was obtained by using the solvent system "water-benzene". In this case with a starting material concentration of 0·15 mole/l, the molecular weight of the polyamide was ~23,000, whereas under the same conditions but with stirring of the initial reagents (~7500 rev/min) a polyamide with molecular weight ~19,000 was obtained. From Fig. 2 it is seen that the largest yield of polyamide (with stirring) (~50 per cent) was obtained at starting material concentration of 0·10 mole/l, whereas without stirring it was obtained at a starting material concentration of 0·25 mole/l. It was also demonstrated that an increased rate of stirring of the reaction mixture increased the yield and the molecular weight of the polyamide (Table 1).

TABLE 1. INFLUENCE OF THE TIME AND INTENSITY OF SHAKING ON THE MOLECULAR WEIGHT AND YIELD OF POLYAMIDE. (CONCENTRATION OF REACTANTS, 0·15 MOL/L.)

Stirring time (min)	Yield % of theory	Spec viscosity of a 0·5% solution in tricresol at 20°C	Molecular weight
	Fast stirring (~ 7500 rev/min)		
0·5	34	0·71	19,000
1·0	45	0·69	18,500
1·5	42	0·71	19,000
3·0	49	0·68	18,400
6·0	46	0·72	19,200
12·0	43	0·73	19,700
	Slow stirring (~ 1000 rev/min)		
3·0	25	0·46	12,500
10·0	32	0·53	14,300
12·0	33	0·46	12,500
90·0	33	0·49	13,200

The data presented show that the yields of polyamides are comparatively low. Evidently this may be explained by the fact that the polyamide being formed is trapped in solvent containing the starting materials, preventing them from touching and preventing further progress of the reaction. As we showed in special experiments, the thickness of the polyamide film virtually did not change in relation to the contact time of the reacting solutions (~30 min) i.e. it follows that the polyamide is poorly permeable to the starting materials.

An increase in the intensity of stirring and use of emulsifiers which are ways of increasing the reaction surface, increased the yield of polymer. Thus the addition of 1 per cent of sodium mersolate raised the yield to 49 per cent compared with 33 per cent which was obtained using similar conditions without the emulsifier.

From Table 1 it is seen that the time of stirring of the initial solution adipyl chloride and hexamethylenediamine shows no material effect on the molecular

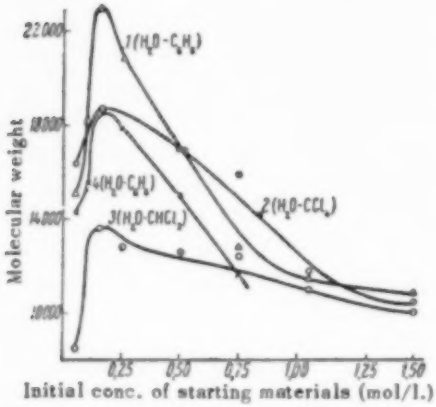

FIG. 1. Change in molecular weight of polyhexamethyleneadipamide in relation to the concentration of starting materials under various conditions. (1,2,3) Polyamide made with out stirring the initial solution; (4) With stirring (−7500 rev/min).

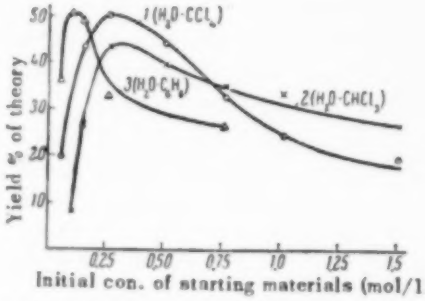

FIG. 2. Change in yield of polyhexamethylenedipamide in relation to the concentration of the starting materials under various conditions. (1,2) Obtained without stirring the initial solution; (3) with stirring (~7500 rev/min).

weight and yield of the polyamide. Since fast stirring is connected with some technical difficulties, later investigations were carried out with stirring at a rate of ~1000 rev/min.

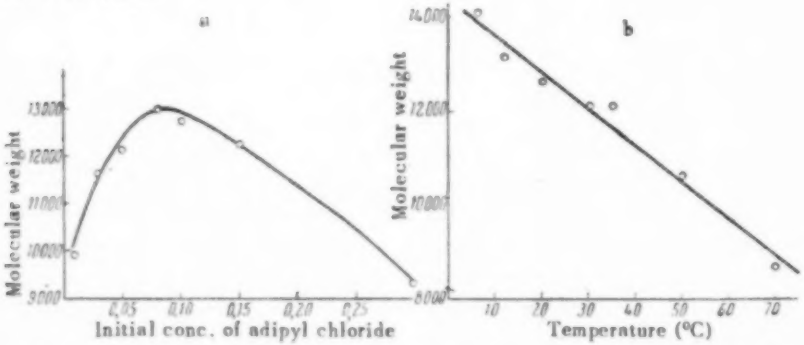

FIG. 3. Change in molecular weight of polyhexamethyleneadipamide in relation to: (a) change in the concentration of adipyl chloride solution (initial concentration of hexamethylenediamine is constant and equal to 0·15 mol/l.); (b) the reaction temperature (concentration of initial reagents 0·05 mol/l.; system benzene–water).

In Fig. 3a, is shown the dependence of the change in molecular weight of the polyamide on the corresponding concentration of starting material. The

concentration of the aqueous hexamethylenediamine solution was constant and equal to 0·15 mole/l in all experiments. The concentration of the adipyl chloride was varied within the limits 0·01 to 0·30 mol/l. As is seen from Fig. 3a the greatest molecular weight was obtained with concentrations of adipyl chloride and hexamethylenediamine of 0·08 and 0·15 mol/l. respectively.

In Fig. 3b is shown the dependence of the change in molecular weight of the polyamide on the reactive temperature. As can be seen from the graph the molecular weight of polyhexamethyleneadipamide increases with decreasing temperature. In the temperature range 6–70° the change in molecular weight follows a linear dependence.

Data on the effects on the nature of the solvents for adipyl chloride is put in Table 2. It is evident from these results that one can successfully use solvents of various types for adipyl chloride.

Data on the influence of various media for absorbing the acid formed during the polycondensation on the molecular weight and yield of the polyamide are presented in Table 3. From these data it is clear that one can use various compounds (NaOH, KOH, $NH_2(CH_2)_6NH_2$, Na_2CO_3) for absorbing the acid formed. Practically identical results were obtained using caustic soda or potash, but on using pyridine for absorbing the acid formed, a lower yield and molecular weight were obtained, obviously on account of the excellent solubility of pyridine both in the aqueous and organic phases.

TABLE 2. INFLUENCE OF THE SOLVENT FOR ADIPYL CHLORIDE IN THE POLYCONDENSATION WITH HEXAMETHYLENE DIAMINE ON THE MOLECULAR WEIGHT AND YIELD

Solvent	Yield %, of theory	Spec. viscosity of a 0·5% solution in tricresol at 20°	Molecular weight
Ethyl ether	41	0·47	12,600
Aromatic hydrocarbons			
Benzene	33	0·47	12,600
Toluene	30	0·47	12,600
p-xylene	29	0·50	13,500
Aliphatic hydrocarbons			
n-Octane	15	0·55	15,200
iso-octane	13	0·57	15,400
Dichloroethane	36	0·51	13,800
Carbon tetrachloride	36	0·53	14,300
Chlorobenzene	40	0·54	14,600

Note. The reaction was carried out with stirring at a rate of 1000 rev/min for 10 min and with the starting materials at a concentration of 0·15 mol/l.

The end groups of the polyamide chains can take part in various reactions as shown below.

$$\ldots -NHRNHCOR'COCl + NH_2RNH_2 \rightarrow \ldots NHRNHCOR'CONHRNH_2 + HCl \quad (1)$$

$$\ldots -NHRNHCOR'COCl + H_2O \rightarrow \ldots -NHRNHCOR'COOH + HCl \quad (2)$$

TABLE 3. INFLUENCE OF THE TYPE OF BASE ON THE MOLECULAR WEIGHT AND YIELD OF POLYAMIDE

Compound	Yield % of theory	Spec. viscosity of an 0·5% solution in tricresol at 20°	Molecular weight
NaOH	33	0·47	12,600
KOH	31	0·49	13,000
Na_2CO_3	22	0·45	12,000
$NH_2(CH_2)_6NH_2$	22	0·43	11,600
C_5H_5N	13	0·22	5900

* See note to Table 2.

Reaction (1) leads to the formation of a terminal amino group which is able to react further, encouraging growth of the chain. As the result of the hydrolysis reaction (2) a terminal carboxylic acid group arises. This is inactive in the conditions given and its formation leads to the cessation of chain growth. It must also be emphasized that the rate of reaction (1) is considerably faster than reaction (2), and it is only thanks to this that it is possible to form polyamides in this way.

On the other hand the process is to some extent the result of the competition between two reactions: the interaction of adipyl chloride with the diamine, and the hydrolysis of the acid chloride, as shown in the scheme.

$$ClCORCOCl \begin{cases} \xrightarrow{NH_2R'NH_2} -CORCONHR'NH- \\ \xrightarrow{+H_2O} ClCORCOOH \text{ and } HOOCRCOOH \end{cases}$$

On hydrolysis the acid chloride loses one group in the first stage to form the monochloride of adipic acid. This compound behaves in the given conditions as a monofunctional addendum, the role of which was shown in detail in the previous report [1] and this leads, by attacking the end of the chain, to a decrease in the molecular weight of the polyamide.

In this way all the factors which are capable of increasing the rate of hydrolysis of the acid chloride must lead to a decrease in yield and molecular weight of the polymer. Indeed, as can be seen from the results presented above, the size of the molecular weight and yield of the polyamide decrease with increase in reaction temperature, and this is a consequence of the increased rate of hydrolysis. The increase in molecular weight on increasing the rate of stirring can be explained from the same point of view. With a greater intensity increases the dispersion of the reaction medium and consequently a greater reagent contact surface is formed. In this way,thanks to the very great rate of interaction of

the acid chloride with the diamine, the acid chloride is rapidly exhausted by incorporation into the polymer and the relative importance of the hydrolysis reaction falls in consequence.

EXPERIMENTAL SECTION

The diamine solution was prepared by dissolving redistilled hexamethylenediamine (b.p. 42°) in distilled water. The calculated quantity of chemically dry sodium hydroxide was added to the diamine solution.

The adipoyl chloride solution was made by dissolving in benzene adipoyl chloride made by Mayer's method [2] from adipic acid and thionyl chloride.

Experimental conditions. Investigations in all cases (excluding the investigation of the effect of the reaction temperature) were carried out at room temperature (~22°) both with and without stirring the initial reagents. Stirring was carried out at different speeds (~7500 and ~1000 rev/min), the number of revolutions of the stirrer being measured with a tachometer.

The film was removed from the interface of the two immiscible liquids in the following way. The alkaline hexamethylenediamine solution was poured into a beaker and then benzene solution of adipyl chloride was carefully poured on to the surface of the first solution. Immediately a film formed at the interface between the liquids, and the film was continuously removed from the reaction medium until the reaction components were used up. The polyhexamethyleneadipamide formed was transferred to a filter washed with acetone to remove benzene, the acid chloride and the diamine, and then with a large quantity of water until completely free from chloride ions, and dried to constant weight in vacuum at 60–80°. The polyhexamethyleneadipamide with molecular weight 12,600 had m.p. 250°.

SUMMARY

(1) The effect of various reaction conditions (time and intensity of stirring, concentration of starting materials, reaction temperature, nature of the solvent and the medium for absorbing acid) on the molecular weight and yield of polyamide was investigated.

(2) When both starting materials (adipoyl chloride and the diamine) were used as solutions of equal concentration, the highest molecular weight was obtained with a concentration of 0·15 mol/l. in the solutions.

(3) The greatest molecular weight of the polyamide was obtained with the following starting material concentrations: adipyl chloride—0·08 mol/l., and hexamethylenediamine—0·15 mol/l.

(4) It was established that an increased stirring intensity favoured an increase in the yield and molecular weight of the polyamide.

(5) It was found that the molecular weight of the polyamide decreased on increasing the reaction temperature.

(6) It was shown that various types of solvent can be successful in the given process.

(7) It was discovered that various bases can be used to absorb the acid produced in the course of the reaction—(NaOH, KOH, $NH_2(CH_2)_6NH_2$, Na_2CO_3, C_5H_5N).

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INVESTIGATION OF ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF SOME IRRADIATED POLYMERS*

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INTRODUCTION

IN the present work electron paramagnetic resonance (EPR) is used to explain certain questions connected with the structure and chemical behaviour of organic radicals which occur in polymers under the action of penetrating irradiation at low temperatures. This question is attracting the attention of more and more researchers, inasmuch as the use of EPR opens up new possibilities for explaining important practical questions about the mechanism of radiation cross-linking and the breakdown of various polymers. Up to the present, the investigations of a number of laboratories [1–3] have produced much valuable information on the structure of the radicals which are formed. However, these works have been concerned mainly with radicals which are stable at room temperature. Such radicals often appear as a result of the interaction of the more active primary atoms and radicals with the molecules of the polymer.

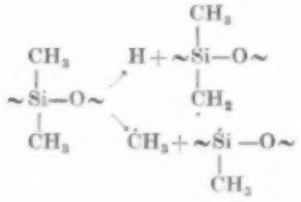
We examined polyethylene, polyvinyl chloride, polyvinylidene chloride, teflon, polydimethyl siloxane, polystyrene, poly*iso*butylene, polypropylene, polyformaldehyde, polymethyl methacrylate, polybutyl methacrylate and natural rubber. The experimental technique and the basic data on the EPR spectra of irradiated polyethylene, teflon, and polyvinyl chloride have been published already [4]. Given below are the data we obtained on the EPR spectra of the other irradiated polymers. For the measurement part of the experiments we used a device which enabled us to make a direct recording of the EPR spectrum in the process of irradiating the specimens under investigation [5]. For these measurements, the specimen was prepared in the form of a tablet and placed in a resonator at the end of a thermocouple. The temperature was maintained by blowing the specimen with a jet of evaporating liquid nitrogen.

* Vysokomol. soedin. **1**: No. 12, 1805–1811, 1959.

EPR SPECTRA OF IRRADIATED POLYMERS

Polydimethyl siloxane $\left[\begin{array}{c} CH_3 \\ | \\ -Si-O- \\ | \\ CH_3 \end{array}\right]_n$. In polydimethyl siloxane irradiated by fast electrons at a temperature of $-150°$ with a dose of 1 megarad, a well resolved spectrum is observed which has seven hyperfine structure components (Fig. 1). An analysis of the number of components the intensity ratios and splitting makes it possible to define two groups of lines—a quadruplet with a splitting of $\pm 0{\cdot}6$ Oe and a triplet with a splitting of $19 \pm 0{\cdot}5$ Oe. The intensity ratio in the quadruplet corresponds completely satisfactorily to 1:3:3:1, i.e. with a binomial coefficient for three equivalent hydrogen atoms. The intensity ratio of the triplet components is not binomial, which is apparently caused by the superposition of an intense singlet on the central component.

As is shown in works [6–8], the effect of irradiation on polydimethyl siloxane leads to the formation of cross links. Breakings of the C—H and Si—C bonds in the polymer are suggested as the primary processes in the formation of free radicals:



Inasmuch as the splitting and the intensity ratio in the quadruplet practically coincides with the value for $\dot{C}H_3$ as known from literature data [9], the quadruplet may be caused by this radical. The spectrum, consisting of three components, should apparently be regarded as the superposition of a singlet from a $\sim\dot{Si}(CH_3)-O\sim$ on a triplet caused by a $\sim Si(CH_3)(\dot{C}H_2)-O\sim$ radical. It is suggested that in the $\sim\dot{Si}(CH_3)-O\sim$ radical the unpaired electron is mainly localized on the Si and O atoms which do not possess nuclear magnetic moments. Therefore, at low temperatures, a hyperfine structure is not observed from hydrogen atoms of the CH_3 group.

With raising the temperature from -150 to $-110°$ a decrease in the intensity of the quadruplet is observed, which corresponds to a decrease in the concen-

tration of $\dot{C}H_3$ radicals. Figure 1 (b, c,) show spectra taken when the specimen was being unfrozen. Refreezing shows (Fig. 1 (d)) that the disappearance of the methyl radicals leads to a certain increase in the intensity of the triplet, i.e. to an

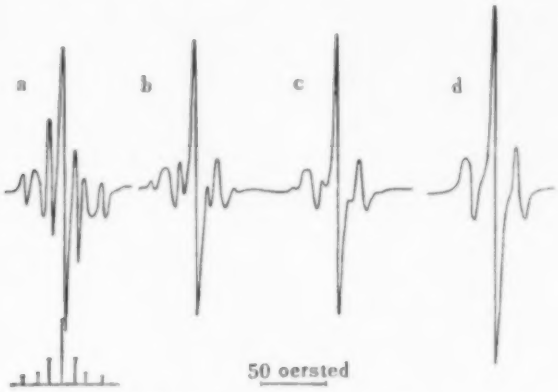


FIG. 1. EPR spectra of irradiated polydimethyl siloxane at: (a) −150°, (b) −125°, (c) −117°, (d) sample refrozen to −150°.

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increase in the concentration of $\sim\mathrm{Si}(\mathrm{CH_3})(\mathrm{CH_2})\mathrm{O}\sim$ radicals. This is apparently caused by reaction of the $\dot{C}H_3$ radical leading to the formation of $\sim\mathrm{Si}(\dot{\mathrm{C}}\mathrm{H_2})(\mathrm{CH_3})\mathrm{O}\sim$ and CH_4 molecules. Actually, the main radiolysis product of polydimethyl siloxane is methane, hydrogen amounts to a smaller part, and only an insignificant part is ethane—the recombination product of two $\dot{C}H_3$ radicals [8]. The formation of H_2 in the course of irradiation can be connected with the analogous reactions of $\dot{H}$ atoms which, however, apparently proceed at lower temperatures, inasmuch as the lines of atomic hydrogen are absent in the EPR spectrum.

Further increase in temperature to room temperature leads to the disappearance of the EPR signal which corresponds to the recombination of all the radicals and to the formation of cross links in the polymer.

With increasing the irradiation dose at low temperatures as the overall intensity of the spectrum grows the quadruplet can be seen less and less distinctly. With a dose of ~10 megarads it is practically invisible because of the superposition of the intense components of the triplet spectrum. Obviously in the given case

the growth of the various radicals takes place by different kinetic laws. This circumstance is also apparently explained by the presence of secondary reactions of $\dot{C}H_3$ radicals and $\dot{H}$ atoms. In the given case, further more detailed EPR study of the kinetic laws of radiolysis of polydimethyl siloxane will be of great interest.

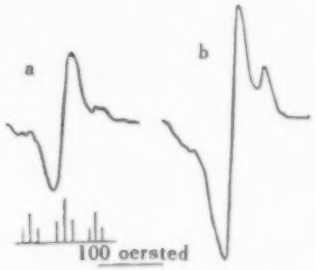

FIG. 2. EPR spectra of irradiated polystyrene at: (a) −25° (b) −195°.

Polystyrene $\left[\begin{array}{l} H \\ | \\ -C-CH_2- \\ | \\ Ph \end{array}\right]_n$. It has been noted before [1, 3] that the EPR spectrum of irradiated polystyrene is a triplet. An analogous spectrum which we obtained at −195° is shown in Fig. 2(b). With increasing the temperature to room temperature a decrease in the intensity of the spectrum takes place and additional splitting (~10 Oe) of the components into three lines is observed (Fig. 2(a)). In the work of Abraham and Whiffen (3) it is suggested that the spectrum of irradiated polystyrene corresponds to the formation in it of $\sim CH_2-\dot{C}-CH_2\sim$ radicals. It is suggested moreover that one proton in each of
|
Ph

the CH_2 groups does not participate in the splitting. However, inasmuch as the spectrum of irradiated polystyrene is analogous to the EPR spectrum of the aromatic compounds irradiated by fast electrons in which the formation of radicals is connected with the breaking of the C−H bond in the benzene ring, it seems to us to be more substantiated to suggest that the triplet which is observed in the polystyrene spectrum should be attributed to the $\sim CH_2-\underset{\cdot}{C}H-CH_2\sim$ radical.
|
Ph

The main splitting (~45 Oe) in the spectrum into a triplet is caused by interaction between the unpaired electron and the two nearest hydrogen atoms of the benzene ring, and the additional splitting (~10 Oe) by two other hydrogen atoms. An analogous spectrum was obtained in the case of poly-α-methyl styrene as well.

Polyformaldehyde $[-CH_2-O-]_n$. At low temperatures (~ −150°) the spectrum

of polyformaldehyde irradiated by fast electrons (a dose of ~60 megarads) is a wide line whose shape is apparently caused by the unresolved hyperfine structure (Fig. 3(a)). With increasing the temperature the spectrum changes, and at −50° a well defined triplet is observed with a splitting of 20±1 Oe (Fig. 3(b)). With further increasing temperature the symmetry in the spectrum is disturbed, which is caused by the superposition of an unsymmetrical line on the triplet (Fig. 3(c)). Complete recombination of the radicals takes place at temperatures of about 0°.

When interpreting the spectrum it should be borne in mind that the number of radical structures with a triplet-type spectrum is extremely limited. Actually, a triplet can only be caused by radicals forming when $\sim CH_2-O-\dot{C}H^2$ and $\sim CH_2-\dot{O}$ chains are broken.

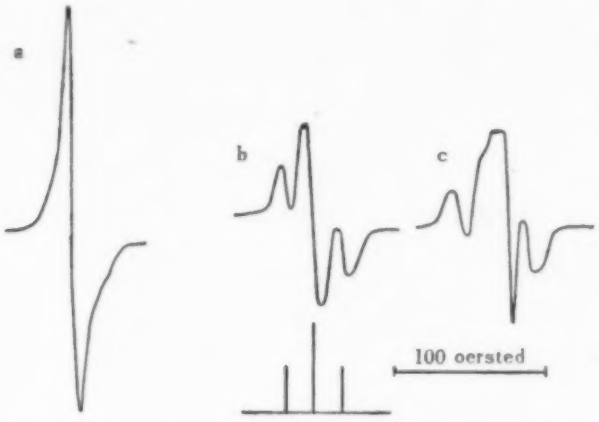

FIG. 3. EPR spectra of irradiated polyformaldehyde at: (a) −150°, (b) −50°, (c) −5°.

Inasmuch as the irradiation was carried out in air, the appearance of the asymmetrical line in the spectrum can be connected with oxygen diffusion and the formation of radicals of the peroxide type (see below).

Thus, the data which we have obtained point to the fact that polyformaldehyde does not cross link during irradiation but destroys. This result of course requires direct chemical confirmation.

Polyisobutylene $[-C(CH_3)_2-CH_2-]_n$. The EPR spectrum of poly*iso*butylene irradiated at −195° (the specimen was irradiated in a nuclear reactor, the dose was ~ 40 megarads) taken at the same temperature is a doublet with splitting of about 20 Oe (Fig. 4). The width of the doublet components is also about 20 Oe, and their intensity is identical. In view of the great width of the doublet components it is not possible to determine the size and width of the splitting. When defreezing the specimen to room temperature the spectrum disappears entirely. The doublet character of this spectrum indicates that in the radicals

which form under the action of irradiation, strong interaction takes place between the unpaired electron and one hydrogen atom. This will take place only if under the action of irradiation at −195° the breaking is mainly of the C—H bond in the CH_2 group of the poly*iso*butylene molecule leading to the formation of $\sim C(CH_3)_2-\dot{C}H\sim$ —type radicals.

FIG. 4. EPR spectra of irradiated poly*iso*butylene taken at −195°.

As is shown in work [10], depolymerization of radicals of this type enables the degradation processes in irradiated polyisobutylene to be explained. In a radical of this type, interaction between the unpaired electron and the hydrogen atom in the α position in relation to the free valency gives a doublet with components of equal intensity. The considerable width of the doublet components

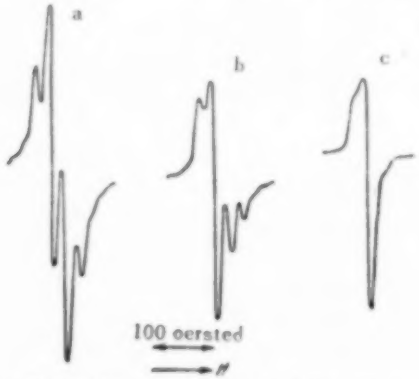

FIG. 5. EPR spectra of irradiated polypropylene: (a) at −150°, (b) (c) change in the spectrum when increasing the temperature by allowing oxygen to be present.

can be caused by the unresolved hyperfine structure which occurs as a result of the interaction between the unpaired electron and the twelve hydrogen atoms of the four CH_3 groups in the β position in relation to the free valency.

Polypropylene $[-CH_2-CH(CH_3)-]_n$. The EPR spectrum of polypropylene irradiated with fast electrons at a temperature of $-150°$ taken at the same temperature apparently consists of eight components with a splitting of 21 ± 1 Oe (Fig. 5(a)).

It is most likely that the spectrum shown in Fig. 5(a) refers to radicals of the $\sim CH_2-\overset{\overset{CH_3}{|}}{\underset{\cdot}{C}}-CH_2\sim$ type, inasmuch as in a radical of this type there are seven equivalent protons in the β position in relation to the free valency.

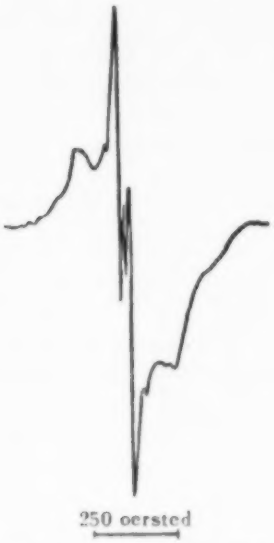

FIG. 6. EPR spectrum of irradiated teflon.

Figure 5(b,c) show how the EPR spectrum of polypropylene changes if the temperature of the specimen is increased by allowing air to come in contact with it. One observes the gradual transition of the spectrum of the alkyl radical into the characteristic asymmetrical line of the hydroxide radical. In analogous conditions we also observed the same transition from the spectrum of the alkyl radical to the single line of the hydroxide radical in the case of powdered polyethylene.

Teflon $[-CF_2-]_n$. The EPR spectra and also the mutual conversions of radicals in irradiated teflon have been described before in works [3, 12, 13]. When irradiating a specimen of teflon with ^{60}Co γ rays *in vacuo* at the temperature of liquid nitrogen with a dose of ~ 60 megarads we were able to see at the same temperature the spectrum shown in Fig. 6. It consists of the wide line in the centre of which at $g = 2{\cdot}003$ at least five hyperfine structure components can be seen. Two components have considerably greater intensity. The splitting

between them amounts to ~38 Oe. When increasing the temperature of the specimen to −78° the intense hyperfine structure components disappear and are not restored with refreezing. The data obtained are preliminary in character. As a hypothesis it can be suggested that the intense doublet corresponds to the EPR spectrum of atomic fluorine. However, it could also be suggested that this spectrum can be caused by radicals occuring in the teflon when the C—C bonds break. Both hypotheses of course require direct experimental confirmation.

Other polymers. The spectrum of irradiated polymethyl methacrylate has already been described in the literature [1, 2]. The spectrum which we obtained for irradiated polybutyl methacrylate was completely analogous to the spectrum of irradiated polymethyl methacrylate. As a result of the complexity of the EPR spectra of irradiated polyvinylidene chloride and natural rubber (unresolved hyperfine structure components) it is not yet possible to draw conclusions about the structure of the free radicals which occur in them under the action of irradiation.

HYDROXIDE RADICALS IN IRRADIATED POLYMERS

At the temperature of liquid nitrogen (−195°) the EPR spectra of the hydroxide radicals in teflon [4], polyethylene and polypropylene are identical and consist of a single asymmetrical line not having a hyperfine structure. The

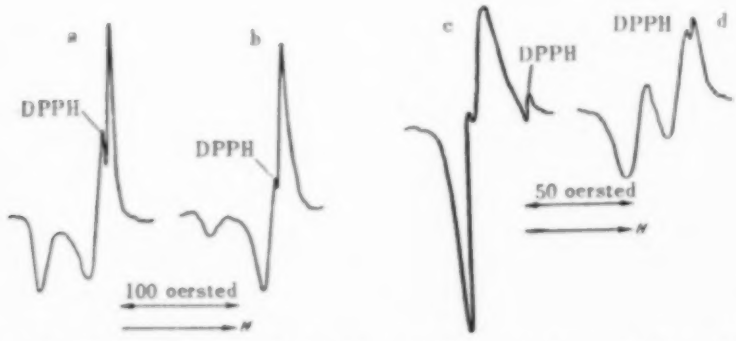

FIG. 7. EPR spectra of the hydroxide radical in a specimen of teflon with orientated polymer chains: (a) (b) perpendicular direction of the polymer chains (a) parallel (b) with magnetic field (−195°); (c) (d) perpendicular direction of the polymer chains (c) parallel (d) with the magnetic field (+20°).

absence of the latter is connected with the fact that the unpaired electron is localized mainly on oxygen atoms whose nuclei have no magnetic moment. The shape of the absorption lines of the hydroxide radicals in polyethylene

and polypropylene undergoes practically no change with temperature right up to +100°. In teflon on the contrary the shape of the line depends substantially upon the temperature [11].

In the light of the explanation suggested for teflon [11] this result means that in the temperature range −200°, +100° the O—Ȯ group in these substances remains stationary. It follows from the result set forth above that the hydroxide radicals in polyethylene and polypropylene have the following structure respectively:

$$\sim CH_2-CH(O\dot{O})-CH_2\sim \quad \text{and} \quad \sim CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}(O\dot{O})-CH_2\sim$$

The low mobility of the group in polypropylene in comparison with teflon could be connected with the greater steric hindrances caused by the presence of the CH_3 group. However, in polyethylene there should be less steric hindrances than in teflon because the dimensions of an H atom are less than those of an F atom. The results obtained can be explained by suggesting that in polyethylene and polypropylene rather strong hydrogen bonds O—O . . . H are formed which hold the O—O groups in a fixed position.

In order to obtain additional data on the structure of the hydroxide radical in teflon we carried out an investigation on specimens with preferred orientation of the polymer molecules along a definite direction. It was established that the shape of the absorption line depends upon the orientation of the specimens in the exterior magnetic field. As can be seen from Fig. 7 (a), (b), (c) and (d), the shape of the line changes more substantially with orientation at room temperature than at the temperature of liquid nitrogen. It can be hoped that research into the dependence between line shape and orientation at various temperatures will make it possible to obtain more accurate data on the character of the movement of the O—O group in relation to the C—O bond.

The authors regard it as their duty to express their thanks to N. Iu. Bubyen, Iu. S. Lazurkin, V. N. Shamshayev, N. N. Bubnov, Ia. S. Lebyedev and A. T. Koritskii for help in carrying out this work.

CONCLUSIONS

(1) The EPR spectra of some polymers irradiated at low temperatures have been studied. On the basis of an analysis of these spectra conclusions have been drawn about the structure of the radicals which are formed during the irradiation.

(2) Conclusions on the chemical conversions of the radicals have been drawn from data on changes in the EPR spectra which take place with increasing temperature.

(3) It has been established that in some polymers the radicals initially formed during irradiation are converted in the presence of oxygen into radicals of the peroxide type.

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CATALYTIC POLYMERIZATION OF OLEFINES—II. THE EFFECT OF ELECTRON-DONOR ADDITIONS ON THE POLYMERIZATION OF PENTENE-1 BY COMPLEX CATALYSTS*†

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AT the present time there are no explanations of the mechanism of polymerization of olefines by complex catalysts based on organoaluminium compounds and titanium halides, nor are there any clear ideas of the means of regulating the process of polymerization both in respect to its rate and in respect to the properties of the resulting polymer. The only questions which have been touched upon are those concerning the influence exerted by the ratio of the catalyst components on the polymerization rate and the molecular weight of the polymers.

The available data on the decisive influence exerted by insignificant quantities of electron-donor substances on the anionic polymerization of dienes [2] in respect of the rate of the process and the microstructure of the polymer chain give reason to suggest that complex Zeigler type catalysts will also prove to be sensitive to additions of substances of this type.

We studied the influence exerted by additions of anisole, diphenylamine and *p*-tolyl mercaptan on the polymerization of pentene-1 by catalysts based on $TiCl_4$ and $Al(C_2H_5)_3$, and also based on the β forms of $TiCl_3$ and $Al(C_2H_5)_2Cl$. Moreover, in the case of the first catalytic system a study was also made of the effect of introducing anisole not only to the ready catalyst (obtained by mixing the components in the absence of the monomer) but also to the individual components before they were mixed.

The polymerization was carried out in single-chamber ampoules; the catalyst components and the additive were measured out of nitrogen tubes, then, *in vacuo*, the pentene and solvent were introduced purified by double distillation from lithium butyl. We determined the yield of polypentane in 20 hr at 20° and the characteristic viscosity of the polymer (compare experiments 1 and 3 with experiments 4 and 5). It is known from the literature however that when

* Vysokomol. soedin. **1**: No. 12, 1821–1823, 1959.

† For part I see [1].

‡ G. I. Filatova and E. P. Iakovleva participated in the experimental part of the work.

polymerizing ethylene by a catalyst based on $TiCl_4$ and $Al(C_2H_5)_3 \cdot CH_3OC_6H_5$ no substantial difference was observed in the polymer yield in comparison with polymerization in the presence of a normal Ziegler catalyst [3]. This incongruity is explained, in our opinion, by the fact that pentene-1 is sensitive to changes in the conditions of polymerization which have no effect on the polymerization of ethylene.

The introduction of anisole together with the monomer to the ready catalyst gives rise to a noticeable decrease in the polymerization rate and correspondingly to a decrease in the polymer yield, and in addition the characteristic viscosity of the polypentene increases slightly. The effect of increased viscosity is more strongly expressed when adding anisole to the system β $TiCl_3$–$Al(C_2H_5)_2Cl$ (*cf.* experiments 10 and 11). If this effect were caused by a simple decrease in the number of active centres due to inactivation of part of them because of additional complexing with anisole, then the molecular weight distribution in the polymer would not differ from the case of polymerization without anisole. However, the precipitation curves on an ultracentrifuge obtained for specimens 10 and 11 of polypentene show a substantially different character of distribution when anisole is added (Fig. 1) *. The presence of a narrower fractional com-

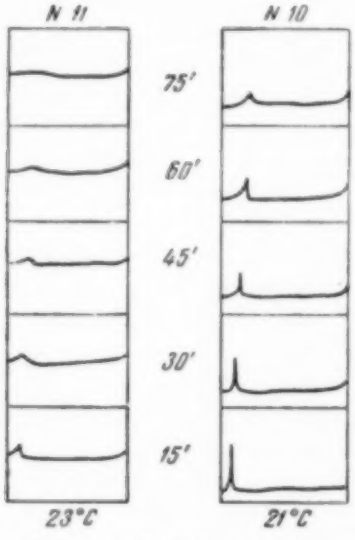

Fig. 1. Sedimentation diagrams of solutions of polymers obtained in experiments 10 and 11.

position indicates a smaller specific value of the reactions of chain breaking. Additions of diphenylamine to the ready catalyst lead to slowing down of poly-

* The sedimentation diagrams were kindly presented to us by M. I. Mosevitskii for which we offer him our thanks.

merization as in the case of anisole; however, with very small ratios of diphenylamine to catalyst the polymer yield increases. The addition of diphenylamine has practically no influence on the characteristic viscosity of the polymer. The

TABLE 1. THE INFLUENCE OF ADDITIONS ON THE POLYMERIZATION OF PENTENE-1 BY COMPLEX CATALYSTS.
(TEMEPERATURE OF EXPERIMENTS 20°, DURATION 20 HR)

No. of experiment	Concentration of reagents (mol/l.)				Molar ratio: addition/Al	Conversion of pentene-1 (%)	$[\eta]$ polypentene
	Complexing addition	$TiCl_4$ or β-$TiCl_3$	$Al(C_2H_5)_3$ or $Al(C_2H_5)_2Cl$	Pentene-1			
1	—	0·067	0·134	4·48	—	29·8	2·05
2*	—	0·075	0·150	5·00	—	48·1	2·55
3†	—	0·069	0·138	4·62	—	30·9	2·55
	Anisole						
4‡	0·526	0·088	0·176	5·84	3·0	2·2	1·7
5§	0·526	0·088	0·176	5·85	3·0	1	0·2
6	0·526	0·088	0·175	5·84	3·0	9·8	2·25
7	0·102	0·102	0·204	6·81	0·5	23·3	3·15
8*	0·038	0·074	0·148	4·92	0·26	13·4	2·25
9	0·016	0·080	0·160	5·36	0·1	8·8	1·85
10⊙	0·138	0·138	0·276	6·90	0·5	44	7·15
11⊙	—	0·147	0·294	7·35	—	63	3·85
	Diphenyl-amine						
12	0·067	0·067	0·134	4·48	0·5	2·0	2·00
13	0·007	0·071	0·142	4·74	0·05	18	1·8
14	0·0014	0·075	0·150	5·00	0·01	43·3	2·45
	p-tolyl-mercap-tan						
15	0·013	0·064	0·128	4·28	0·1	67·2	1·25
16	0·067	0·067	0·134	4·48	0·5	14·3	2·3

* Duration of the experiment 40 hr; † 1,72 mol/l. benzene added; ‡ Anisole introduced to a solution of $TiCl_4$; § Anisole introduced to a solution of $Al(C_2H_5)_3$; ⊙ Catalyst $TiCl_3$-$Al(C_2H_5)_2Cl$.

introduction of *p*-tolyl mercaptan in a quantity of 0·5 moles/mole of aluminium alkyl retards the polymerization while not influencing the viscosity of the polymer. With a smaller quantity of *p*-tolyl mercaptan a greater polymerization rate was observed at the beginning of the process as well as an increase in polymer yield, but the polymer had a lower viscosity. Since diphenylamine and *p*-tolyl mercaptan were employed in the form of solutions in benzene, a check

was made of the influence exerted by the presence of benzene on polymerization by a normal catalyst. It was found that benzene has no influence on the course of polymerization or on the viscosity of the polymer (experiment 3).

It is believed that further study on the influence of the addition to Ziegler catalysts of substances capable of complex formation with these catalysts may prove useful for explaining the structure of the active centre.

CONCLUSIONS

It has been found that additions of diphenylamine and *p*-tolyl mercaptan in low concentrations to complex catalysts of the Ziegler type lead to increase in the polymerization rate.

With high concentrations of diphenylamine and *p*-tolyl mercaptan, as well as with additions of anisole, a slowing down of the polymerization rate was noted with no substantial change in the molecular weight.

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ELECTRON PARAMAGNETIC RESONANCE STUDY OF POLYMERIZATION IN THE ACRYLONITRILE-MAGNESIUM SYSTEM OBTAINED BY MOLECULAR BEAM CONDENSATION*

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IN works [1,2] it was shown that when condensing the molecular beams of certain inorganic substances and monomers together on very cold surfaces, it is possible to obtain systems in which the polymerization of these monomers proceeds at extremely low temperatures at a very fast rate.

Moreover, in a number of cases, with dispersion to molecular dimensions, inorganic substances, which in the state of formed crystals are in no way capable of inducing polymerization, are found to be active polymerization initiators and catalysts.

One variation of such systems is a frozen molecular mixture of metallic magnesium with monomers of the vinyl series of the acrylonitrile or methylmethacrylate type obtained by condensing together *in vacuo* on a surface cooled with liquid nitrogen [1]. In these systems, polymerization commences at temperatures considerably below the melting point of the monomers and proceeds at a fast rate, sometimes with explosive velocity. Thus, for the molecular mixture acrylonitrile - Mg, the starting temperature of polymerization lies in the region of $-140°$C (the melting point of acrylonitrile is $-82°$), and for the mixture methylmethacrylate–Mg it lies in the region of $-100°$ (the melting point of methylmethacrylate is $-50°$).

The mechanism of the rapid polymerization of these monomers, which at the given temperatures are in the solid state, is of considerable interest. It is unlikely that the development of the reaction chain in a frozen monomer takes place by the co-ordination or ionic mechanism involving an ion pair. Such a process ought to be connected with successive introduction of molecules of the monomer at the site of the active ion pair or the co-ordination complex, and this requires a certain mobility of the particles in the polymerizing system. In actual fact, to achieve polymerization by any of these mechanisms what is required is at least the migration of a magnesium ion along the growing chain.

* Vysokomol. soedin. 1: No. 12, 1859–1861, 1959.

Otherwise renewal of the active co-ordination complex or ion pair will not be able to take place at the end of the chain. At low temperatures in a solid monomer such migration is scarcely possible. In any case, it could not be characterized by a speed commensurate with the rate of polymerization observed.

The difficulties do not arise if one assumes that the polymerization of the frozen solid monomer takes place by a radical mechanism. In this case, it is easy to imagine the growth of the polymer chain as the migration of the free valency along a system of previoulsy ordered monomer molecules. Thanks to this prior ordering, the polymerization can take place at extremely high rates and can be characterized by lower negative values of entropy of activation.

In order to check the assumption made above we made use of electron paramagnetic resonance (EPR). This enabled us to make direct judgement as to the presence of free radicals in the polymerizing system. With this object, a modified version of the reaction vessel described in work [1] (Fig. 1) was used. The

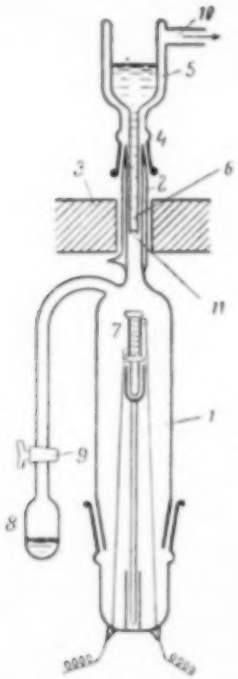

FIG. 1. Diagram of the reaction vessel.

instrument was made from quartz and consisted of an elongated vessel 1, ending at the top in a tube 2, with thin double walls which entered into a 15 mm aperture in a resonator 3. The double walls of tube 2 passed into a hermetic joint 4, by means of which the tube was connected with a trap 5, ending in a thin-walled

finger 6, which reached as far as the centre of the resonator. A quartz electric furnace 7, was fixed into vessel 1, and the magnesium was sublimated from this furnace. Vapours of the monomer came from the ampoule 8, and their supply rate was regulated by a cock 9. The experiments were conducted with the instrument continuously evacuated to a high vacuum through branch-piece 10. In this way, the vapours of the monomer and magnesium were condensed on finger 6, which was cooled with liquid nitrogen in the depression 11, accurately installed at the centre of the resonator. After a definite period of time, EPR spectra were recorded directly in the process of sublimation. The EPR was measured with a device analogous to the one described in work [3].

The absorption signal was observed immediately after the mixture of vapours began to condense. (It was established by check experiments that separate condensation of magnesium vapours and acrylonitrile vapours does not lead to the appearance of an EPR signal in the conditions of the experiment). The spectrum obtained is illustrated in Fig. 2. It is a singlet with a line width of the order of 16 Oe. By comparison with a specimen of 1,1-diphenyl-2-picryl hydrazyl (DPPH) of known concentration, it was established that the amount of radicals in the system is of the order of 10^{18} rad/g. The value of the g-factor of the radicals which were discovered was close to the value of the g-factor of DPPH (2.0036).

Polymeric radicals which form when polymerizing acrylonitrile have been studied in a number of works. The most detailed investigations have been made by Ingram *et al.* [4], who studied the photopolymerization of acrylonitrile at room temperature and above. It was shown in particular that the spectrum of the radicals forming with photopolymerization is characterized by a singlet with a line width of 28 Oe. The smaller width of the absorption line of the acrylonitrile radical in our experiments can apparently be connected with the greater degree of order which arises with polymerization in a system which is at a temperature near to that of liquid nitrogen. We, like Ingram, did not manage to resolve the hyperfine structure of the acrylonitrile radical. Possibly the reason for this is the peculiar properties of the radical, or the insufficient sensitivity of the apparatus.

In our experiments when increasing the temperature to room temperature we did not observe any destruction of the radicals or any noticeable change in their concentration. This means that the polymeric radicals which have formed are "captured" in the structure of the solid polymer.

We also studied the EPR spectrum after the polymer had been in contact with the oxygen of the air for 25 min. This spectrum is given in Fig. 3. Changes in the spectrum can be noted which are probably connected with a change in the chemical nature of the radicals. This is also indicated by a certain increase in the g-factor which is found when recording together the spectra of DPPH and the radical under investigation. The question of the nature of this radical requires further study.

Thus, the data which we obtained testify to the fact that the low-temperature polymerization of a molecular mixture of frozen acrylonitrile and magnesium takes place by a radical mechanism. Radicals are apparently formed during interaction between the vapours of the monomer and magnesium, for example:

$$CH_2=\underset{\displaystyle C\equiv N}{\underset{|}{CH}}+Mg-\dot{M}g-\bar{C}H_2-\underset{\displaystyle C\equiv N}{\underset{|}{\dot{C}H}}$$

These radicals together with excess monomer are condensed on a surface cooled with liquid nitrogen and initiate polymerization in the frozen mixture.

FIG. 2. EPR spectrum of the acrylonitrile radical.

FIG. 3. EPR spectrum after the polymer had been in contact with the oxygen from the air for 25 min.

In the future it is intended to make a more detailed study of the properties of the radicals which arise in the given system and to investigate by electron paramagnetic resonance other systems obtained by the molecular beam method.

CONCLUSIONS

Polymerization in a frozen molecular mixture of acrylonitrile and magnesium obtained by the molecular beam method was studied by means of electron paramagnetic resonance. Polymerization in this system takes place by a radical mechanism. Polymerization is apparently initiated by radicals which form during interaction between the vapours of magnesium and acrylonitrile and condense together with excess monomer on the cooled surface.

Translated by J. J. CORNISH

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ABSTRACTS FROM PAPERS PUBLISHED IN *VYSOKOMOLEKULIARNYE SOEDINENIIA* Vol. 1, No. 10, 1959*

SYNTHESIS AND POLYMERIZATION OF HEXAMETHYLENEDIMETHACRYLAMIDE

V. V. Korshak, K. K. Mozgova, Vysokomol. soedin. **1**: No. 10, 1457–1461, 1959.

HEXAMETHYLENEDIMETHACRYLAMIDE $CH_2=C(CH_3)CONH\ (CH_2)_6NHCO-C(CH_3)=CH_2$ is formed in approximately 30 per cent yields on interaction between methacryl chloride and hexamethylenediamine. The block polymerization of hexamethylenedimethacrylamide at 115–120° leads to formation of the trimer of decomposition temperature *ca.* 400°C. On block copolymerization of hexamethylenedimethacrylamide and methylmethacrylate or styrene colourless, transparent trimer are formed with decomposition temperature within the limits of 300–380°C. When hexamethylenedimethacrylamide is polymerized in the presence of the polyamide anide G-669 in alcoholic solution with a large quantity of initiator a powdered trimer is obtained with decomposition temperature about ~ 400°C.

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QUANTITATIVE DETERMINATION OF COOH AND H_2O IN CELLULOSE BY THE METHOD OF INFRA-RED SPECTROSCOPY

I. N. Ermolenko, S. S. Gusev, Vysokomol. soedin. **1**: No. 10, 1462–1468, 1959.

THE validity of the earlier proposed pressing method for the quantitative analysis of oxidized cellulose has been demonstrated on the example of the quantitative determination of carboxyl groups and sorbed water in dicarboxycelluloses not containing Ketonic groups. The absorption coefficient of the carboxyl CO band of oxidized cellulose is 860 ± 10 per cent (l/cm g/equ/100 g) and is practically independent of the nature of the cellulose material. Simultaneously present H_2O and COOH groups may be quantitatively determined.

HETEROCHAIN POLYESTERS – XXIV. ON SOME POLYESTERS OF DIATOMIC PHENOLS

V. V. Korshak, S. V. Vinogradov, Vysokomol. soedin. **1**: No. 10, 1482–1486, 1959.

POLYESTERS of diatomic phenols and sebacic and adipic acids and mixed polyesters of diatomic phenols of the following systems: hydroquinone-diane-*tere*phthalic acid, diane-*tere*phthalic and *iso*aphthalic acids and hydroquinone-diane-*tere*phthalic and *iso*phthalic acids have been synthesized and investigated. The effect of the reagent structure and of the mixed polyester composition on the physical properties of the polyesters has been discussed.

POLYMERIZATION OF GLYCIDE ETHERS – I. POLYMERIZATION OF PHENYLGLYCIDE ETHER UNDER THE ACTION OF ALKALINE CATALYSTS AND INITIATING AGENTS

M. F. Sorokin, L. G. Shode, Vysokomol. soedin. **1**: No. 10, 1487–1492, 1959.

IN the work a new method has been proposed for the formation of phenylglycide ether polymers, using alkaline catalysts (KOH, C_2H_5ON, NaOH) and additions of initiating sub-

* English abstracts reprinted from Vysokomol. soedin. **1**: No. 10, 1959.

stances capable of opening up the oxide ring. The polymerization rate has been shown to be dependent upon the type and quantity of catalyst and upon the amount of initiator, as well as upon the reaction temperature.

A number of the polymers was isolated, fractionated and analyzed. Fraction I, crystalline with a melting temperature 98–130°, constituted 3–14 per cent of the over-all mass of the polymer. Fraction II, a viscous resin, depending upon the reaction conditions has a molecular weight 1000–3700 and constituted 70–93 per cent of the over-all polymer weight.

The method of polymerization suggested may be of general significance for the synthesis of polymers from oxides.

HYDROLYSIS OF DIMETHYLDICLOROSILANE BY SODIUM ALUMINATE SOLUTIONS

I. K. Stavitskii, S. N. Borisov, Vysokomol. soedin. **1**: No. 10, 1496–1501, 1960.

In a strongly alkaline medium, hydrolysis of dimethyldichlorosilane by aqueous sodium aluminate solutions is accompanied by the formation of various polydimethylalumasiloxanes. Their consistency depends upon the initial Si:Al ratios.

Low molecular pseudo-rubber unstable polymers that do not manifest properties characteristic of organosilicon elastomers are formed as the result of alkaline polymerization of the oily polydimethylalumasiloxanes.

POLYMERIZATION AND COPOLYMERIZATION OF FLUORINATED STYRENES

A. R. Gantmakher, Yu. L. Spirin, S. S. Medvedev, Vysokomol. soedin **1**: No. 10, 1526–1530, 1960.

The polymerization and copolymerization of various fluorine-substituted styrenes have been investigated. It has been shown that substitution of ring hydrogen atoms by the F and CF_3 groups little affected the reactivity of the styrene molecule. The presence of fluorine atoms in the β position in the vinyl group lowers the relative reactivity of the styrene molecule and the rate of its polymerization.

The rate of interaction of a number of fluorinated styrenes ($\beta;\beta,\beta;\alpha,\beta;\alpha,\beta,\beta,\alpha$- trifluoromethylstyrene etc.) with their own radicals have been found to be greatly diminished because of the repulsive forces appeqring on interaction between the radical and molecule of the fluorinated monomer.

The reactivity of various fluorinated styrenes with respect to the styrene radical has been determined by the method of copolymerization.

INVESTIGATIONS INTO THE THERMAL DEGRADATION OF CONDENSATION RESINS—I. THE THERMAL DEGRADATION OF EPOXIDE RESINS

M. B. Neiman, L. I. Gotubenkova, B. M. Kovarskaia, A. S. Strizhkova, I. I. Levantovskaia, M. S. Akutin, V. D. Moiseev, Vysokomol. soedin. **1**: No. 10, 1531–1537, 1960.

The epoxide resin ED-6 has been shown to decompose noticeably at temperatures above 240° with an effective activation energy 34,000 cal/mole. Liquid decomposition products comprising low molecular fractions are formed. Among the decomposition products carbon monoxide, methane, formaldehyde and water have been shown to appear. A radical mechanism for the degradation of the resin has been proposed, beginning with cleavage of the epoxide group.

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ELECTRONOGRAPHIC INVESTIGATION OF FLUORINATED POLYMERS

S. S. Leschenko, Y. L. Karpov, V. A. Kargin, Vysokomol. soedin. **1**: No. 10, 1538–1546, 1960.

In the paper the results are presented of structural studies of polytetrafluoroethylene, polyvinylidenefluoride and vinylidene fluoride–tetrafluoroethylene copolymers by the electronographic method. Polyvinylidenefluoride and polytetrafluoroethylene have been shown to be crystalline polymers, the molecules of which possess a three-dimensional spiral, the units being located in a regular zig-zag fashion. Vinylidene fluoride and tetrafluoroethylene copolymers are crystalline polymers with a rhombic elementary cell, their structure remaining constant over a rather broad range of change in monomer unit ratios. It differs from the structure of crystalline polyvinylidenefluoride and polytetrafluoroethylene.

SOME PROPERTIES OF STARCH AND METHYLMETHACRYLATE GRAFT COPOLYMERS

V. A. Kargin, N. A. Plate, E. P. Rehbinder, Vysokomol. soedin. **1**: No. 10, 1547–1551, 1960.

On ozonizing starch and amylose with subsequent polymerization of methylmethacrylate, graft starch and methylmethacrylate and amylose and methylmethacrylate copolymers are formed containing 80–90 per cent polymethylmethacrylate. The glass temperature of such systems is determined by the glass temperature of polymethylmethacrylate.

In amylose–methylmethacrylate, graft copolymers containing 80 per cent polymethylmethacrylate the structural ordering of one of the components, amylose, may be rested.

VISCOMETER FOR DETERMINING THE VISCOSITY OF SOLUTIONS OF HIGH MOLECULAR COMPOUNDS

S. R. Rafikov, Vysokomol. soedin. **1**: No. 10, 1558–1560, 1960.

A description has been given of a suspended level Ubbelohde type viscometer, easy to make and convenient in manipulation, for use with small amounts of substance.

CERTAIN FEATURES OF THE DESTRUCTION OF ANNEALED POLYSTYRENE

M. I. Bessonov, E. V. Kuvshinskii, Vysokomol. soedin. **1**: No. 10, 1561–1564, 1960.

Annealed specimens of polystyrene during stretching disrupt along large single cracks. The cracks are filled with loose material apparently consisting of preliminarily de-formed "packets" of molecules separated into layers. The material filling in the cracks along which rupture took place may be isolated from the rupture surface and separately investigated.

CARBOCHAIN POLYMERS AND COPOLYMERS—XVIII. SYNTHESIS OF GRAFT COPOLYMERS FROM POLYMETHYLMETHACRYLATE AND MIXED POLYESTERS

H. S. Kolesnikov, Tsen Han-Min, Vysokomol. soedin.**1**: No. 10, 1565–1569, 1959.

Graft copolymers have been prepared by the interaction in chlorobenzene of polymerthylmethacrylate and mixed polyesters and their properties have been investigated. Graft copolymers from polymethylmethacrylate and mixed crystalline polyesters possess a *quasi*-crystalline structure. The grafting of an amorphous polyester to polymethylmethacrylate leads to the formation of an amorphous graft copolymer.

PREPARATION OF GRAFT COPOLYMERS OF CELLULOSE BY IRRADIATION WITH ^{60}Co

Kh. U. Usmanov, B. I. Aikhodzhaev, U. O. Azizov, Vysokomol. soedin. **1**: No. 10, 1570, 1959.

THE grafting of acrylonitrile to cellulose by irradiation of the mixture by γ-rays of a ^{60}Co source with an integral dose of $1–10^6$ r has been studied. It has been shown that the grafting takes place only when nitrile has been preliminarily dissolved in a liquid wetting well the cellulose.

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PREPARATION OF GRAFT COPOLYMERS—IV. THE GRAFTING OF STYRENE TO POLYAMIDES

V. V. Korshak, K. K. Mozgova, M. A. Shkolina, Vysokomol. soedin. **1**: No. 11, 1573–1579, 1959.

GRAFT copolymers have been obtained from styrene and ozone treated polycaprolactam and anide G-669 films. The mechanical and thermomechanical properties, the melting temperatures, viscosities, elementary composition, wetting by various solvents and the solubility have been shown to change in comparison with those of the initial polymers.

A graft resin has been isolated and investigated that proved to be close to polystyrene in its elementary composition.

LIGHT SCATTERING AND VISCOSITY OF POLY-β-VINYLNAPHTHALENE IN BENZENE

V. E. Eskin, O. Z. Korotkina, Vysokomol. soedin. **1**: No. 11, 1580–1585, 1960.

THE intrinsic viscosity and light scattering of 11 fractions of poly-β-vinyl-naphthalene have been measured at 17°C. The relationship $(\eta) = 0{,}17 \times 10^{-4} M^{0.8}$ has been established, valid for the range of molecular weights (0,1–1,0). Determinations have been made of the second virial coefficients. The assumption that the poly-β-vinylnaphthalene chains possess considerable thermodynamic rigidity has been grounded.

HETEROCHAIN POLYESTERS—XXV. INVESTIGATION INTO POLYCONDENSATION IN A THIN LAYER

V. V. Korshak, V. A. Zamiatina, N. I. Bekasova, Vysokomol. soedin. **1**: No. 11, 1586–1592, 1959.

POLYCONDENSATION in a static thin layer has been studied in a nitrogen medium under atmospheric pressure, using polyethyleneterephthalate as example. The rate of reaction was determined from the time change of viscosity of the polyester.

Within the limits investigated, from 0·35 mm to 1·3 mm, the rate constant of the reaction varied regularly as the inverse thickness of the layer.

The polycondensation kinetics were investigated over the temperature range 244–296° in the presence of the catalysts Al_2O_3, $Zn(CH_3COO)_2$, $Ca(OH)_2$ and in the absence of a catalyst at a layer thickness 1mm. The activation energy calculated varied within the limits 11–14 kcal/mole, depending upon the activity of the catalyst, whereas on polycondensation in an apparatus with a stirrer, according to earlier experiments carried out by the authors, it was 35 kcal/mole.

It was concluded that polycondensation in a thin layer is a reaction of the second order and proceeds at a considerably higher rate than under ordinary conditions, owing to easier evaporation of ethylene glycol and improved conditions of heat transfer.

* English abstracts reprinted from Vysokomol. soedin. **1**: No. 11, 1959.

THE HYDROGEN BOND AND THE POLYMERIZATION CAPACITY OF *o*-, *m*-, AND *p*-SUBSTITUTED N-PHENYLMETHACRYLAMIDES—IV

T. A. Sokolova, G. M. Chetyrkina, V. N. Nikitin, Vysokomol. soedin. **1**: No. 11, 1599–1603, 1959.

It was established earlier by the authors that owing to molecular association *m*-and *p*-substituted N-phenylmethacrylamides polymerize more slowly than their *o*-isomers in which intermolecular hydrogen bonds are absent.

In the present work a new group of compounds of this series, namely *o*-and *p*-diphenylmethacrylamides (*o*-, and *p*-DPMA) and o-, *m*-, and *p*-chlorophenylmethacrylamides (*o*,*m*,n,-CPMA) have been investigated. The monomers were synthesized by reaction of corresponding amines with methacryl chloride in the presence of triethylamine. *p*-DPMA has been prepared and described for the first time. The presence of intermolecular hydrogen bonds has been revealed in all these compounds with the aid of infra-red absorption spectra; however in the case of *o*-DPMA and *o*-CPMA they are easily ruptured, whereas with the *m*- and *p*-isomers they are preserved in the melt. Hence on bulk polymerization at temperatures above the monomer melting temperature, the rate is higher for *o*-DPMA and *o*-CPMA than for their isomers.The absence of hydrogen screening of the NH group in *ortho* compounds (in the crystalline state) may be explained by the small atomic volume of chlorine in *o*-CPMA and by deviation from coplanarity of the second benzene nucleus in *o*-DPMA.

THE SOLUBILIZATION EFFECT AND THE CONFIGURATION OF PROTEIN MOLECULES IN SOLUTION

V. A. Pchelin, V. N. Izamailova, N. I. Seraia, Vysokomol. soedin. **1**: No. 11, 1617–1624, 1959.

The solubilization of nitrobenzene by gelatine solutions has been studied at different pH values of the medium, concentrations and temperatures. The solubilization–pH correlation at 20°C has a maximum at the isoelectric point, owing to the globular state of the gelatin in solution. There is on solubilization in solutions of thermolysed gelatin even at 30°C. The experimental material obtained shows that the solubilization effect may serve the basis of determining the configuration of protein molecules in solution and for observing changes in the configuration under various conditions.

SYNTHESIS OF NEW CELLULOSE AND OTHER POLYSACCHARIDE DERIVATIVES—III. SYNTHESIS OF CARBOXYMETHYLCELLULOSE AND POLYENANTHAMIDE GRAFT COPOLYMERS

Sun Tun, V. A. Derevitskaia, Z. A. Rogovin, Vysokomol. soedin. **1**: No. 11, 1625–1629, 1959.

A method has been developed for the synthesis of polyamide-carboxylated polysaccharide graft copolymers by the polycondensation of methyl aminoenanthate in the presence of the methyl ester of carboxymethylcellulose. A technique has been devised for separating the graft copolymer from the homopolyamide formed as a side product.

The mean degree of polycondensation of the polyamide in the graft copolymer side chains has been determined.

SYNTHESIS OF NEW CELLULOSE AND OTHER POLYSACCHARIDE DERIVATIVES—IV. THE SYNTHESIS OF CARBOXYMETHYLCELLULOSE AND POLYCAPROLACTAM GRAFT COPOLYMERS

Z. A. Rogovin, U Zhun-zhui, Vysokomol. soedin. **1**: No. 11, 1630–1633, 1959.

A METHOD of synthesis of the amide of caprolactam and carboxymethylcellulose by interaction of the chloroanhydride of carboxymethylcellulose with a solution of Na-caprolactam in N-methylcaprolactam solution has been developed. The carboxymethylcellulose-caprolactam graft copolymer has been synthesized by the interaction of carboxymethylcellulose chloranhydride with caprolactam in the presence of Na-caprolactam. In this method of synthesis no side product formation of the homopolyamide takes place. The mean degree of polymerization of the caprolactam in the side chains of the graft copolymer has been determined.

POLYMERS WITH CONJUGATED BONDS IN THE MACROMOLECULAR CHAINS—III. ON POLYAMINOQUINONES

A. A. Berlin, N. G. Matveeva, Vysokomol. soedin. **1**: No. 11, 1643–1646, 1959.

POLYAMINOQUINONES, a new class of compounds, have been synthesized by the interaction of chloranil and benzidine or hexamethylenediamine. The compounds are capable of polymer-homologous conversions owing to the labile chlorine atoms in the quinone residues and form polymer complexes with metal salts. Aromatic polyaminoquinones and their complexes have been found to possess paramagnetic properties and exhibit narrow and broad lines in the ER spectra, bearing evidence of the presence of unpaired electrons.

THE INTERACTION OF CARBOXYLATED RUBBER WITH ε-CAPROLACTAM

I. A. Tutorskii, Z. Smelyn, B. A. Dogadkin, Vysokomol. soedin. **1**: No. 11, 1652–1654, 1959.

ON heating in a press at 200–220° a mixture of butadienestyrene rubber containing 1% methacrylic acid with ε-caprolactam the latter is found to add to the rubber. The product swells to a limited extent in benzine and swells in water, indicating an increase in polarity of the rubber as a result of the reaction.

VISCOSITY STUDIES OF CONCENTRATED METHACRYLIC ACID-STYRENE COPOLYMER SOLUTIONS

Yu. S. Lipatov, P. I. Zubov, Vysokomol. soedin. **1**: No. 11, 1655–1658, 1959.

THE change in specific viscosity with temperature has been studied for methacrylic acid–styrene copolymers with an acrylic acid content of 47·9 and 70·3 per cent. The specific viscosity of the solutions investigated to a concentration of 8 per cent has been shown to diminish with increasing temperature. The partial neutralization of the carboxyl groups does not change the temperature dependence of the viscosity but the values of the specific viscosities at 20° increase in comparison with the viscosities of solutions of copolymers not containing COONa groups .The results obtained have been compared with those of earlier studies on methacrylic acid solutions and are explained from the standpoint of the partial lowering of the copolymer solubility on heating and the effect of chain flexibility on the formation of intra-and intermolecular bonds.

PLASTICIZATION OF CRYSTALLINE POLYMERS—I. PLASTICIZATION OF ISOTACTIC POLYSTYRENE AND POLYETHYLENETEREPHTHALATE

V. A. Kargin, T. I. Sogolava, G. Sh. Talipov, Vysokomol. soedin. **1**: No. 11, 1670–1677, 1959.

In this study an investigation has been carried out into the action of various plasticizers on the thermomechanical properties of crystalline polymers. The introduction of low molecular compounds has been shown to widen the interval between the glass and melting temperatures. The lowering of the glass temperature obeys the same rule of partial volumes as in the case of non-polar amorphous systems.

STUDIES IN THE MECHANO-CHEMISTRY OF POLYMERS—VIII. DEGRADATION OF POLYDIMETHYLSILOXANE BY THE ACTION OF ULTRASONIC WAVES

A. A. Berlin, A. M. Dubinskaia, Vysokomol. soedin. **1**: No. 11, 1678–1684, 1959.

A study has been made of the effect on the rate of ultrasonic degradation of polydimethylsiloxane of a number of factors, namely, the US intensity, concentration of the solutions, type of solvent, medium. The rate constants of degradation for various US intensities have been calculated. It has been found that in the degradation of polydimethylsiloxane macroradicals are absent. The suggestion has been made that degradation of polysiloxane by ultrasonic is of a molecular nature.

SYNTHESIS AND INVESTIGATION OF POLYUREA

O. I. Fedotova, I. P. Losev, N. I. Skripichenko, M. A. Okunchikova, L. V. Bykova, M. I. Shtilman, Vysokomol. soedin. **1**: No. 11, 1685–1690, 1959.

A number of new polyureas has been synthesized by the addition of di*iso*cyanates to diamines. The available aromatic diamines, *m*-tolylenediamine, *p*-xylylenediamine benzidine, 4,4'-diaminodiphenylmethane, 4,4'-diamino-3,3'-methyldiphenylmethane, N,N'-diethyl-4,4'-diamino-3,3'-dimethyldiphenylmethane, N,N'-dipropyl-4,4'-diamino-3,3'-dimethyldiphenylmethane, 4,4'-diaminodiphenylsulfide, etc., were used. The aliphatic and aromatic diisocyanates 1,6-hexamethylenedi*iso*cyanate, 2,4'-tolylenedi*iso*cyanate and 4,4'-di*iso*cyanate-3,3'-dimethyldiphenylmethane were used as second components.

The formation of polyurea from aromatic diamines proceeds at high speeds and with an exothermal effect already at room temperatures. In order to investigate the kinetic aspect of the reaction it was carried out at −3 and −20°C. It was found that the polymer yield molecular weight and melting interval increase and the *iso*cyanate number decreases with time. The dependence of the reaction rate on the concentration was also established at these temperatures. Thus on lowering the concentration from 20 to to 5 per cent the rate fell approximately 6 times.

Of the polyureas synthesized a number was shown to be capable of practical application as forming materials, as well as sheets and films with high ultimate strength and dielectric properties.

ON VINYLCROTONATE AND ITS POLYMER

E. N. Rostovskii, A. N. Barinova, Vysokomol. soedin. **1**: No. 11, 1707–1712, 1959.

A study has been made of the polymerization of vinyl α-crotanate in the presence of a radical type of initiator. In the polymer obtained in ethyl acetate besides the crotonate

group lactone cycles were present, bearing evidence of the cyclic mechanism underlying the polymerization process. On photopolymerization in carbon tetrachloride the low molecular telomer was obtained in high yields.

The original vinylcrotanate monomer was synthesized by the vapour phase contact method. α-Crotonic acid was obtained from the aldol; besides the α-(*trans*)isomer, the β-(*cis*)isomer was also isolated.

It has been shown that the degree of unsaturation in the vinyl and acyl groups of vinylcrotonate may be determined separately.

POLYMERIZATION OF SOME MONOMERS DURING DISINTEGRATION OF INORGANIC SUBSTANCES

N. A. Plate, V. V. Prokopenko, V. A. Kargin, Vysokomol. soedin. **1**: No. 11, 1713–1720, 1959.

THE intensive mechanical disintegration of a number of inorganic compounds of amorphous or crystalline structure-quartz, carbon black, graphite, sodium chloride, metallic iron and magnesium, zinc dioxide, calcium fluoride, etc., in a vibro mill in a medium of common monomers leads to polymerization of the latter. Initiation of the polymerization is carried out by free radicals or active ions in the new surfaces of the solids formed during their disintegration.

The technique of polymerization developed permits a wide range of graft copolymers to be obtained on the basis of organic and inorganic components.

MECHANISM OF THE FORMATION OF POLYMER CRYSTALS – I

V. A. Kargin, T. A. Koretskaia, Vysokomol. soedin. **1**: No. 11, 1721–1723, 1959.

THE globular form of polyethylene has been obtained and it has been shown that crystallization does not take place in that case. Crystallization has been found to be associated with packet structures.

POLYCONDENSATION IN THE SOLID PHASE – II. SOLID PHASE POLYCONDENSATION OF ζ-AMINOENANTHIC ACID IN THE PRESENCE OF CATALYSTS

A. N. Volokhina, G. I. Kudriavtsev, Vysokomol. soedin. **1**: No. 11, 1724–1732, 1959.

THE use of catalysts in solid phase polycondensation proceeding at lower temperatures and lower rates than in the liquid phase of a solution or melt is of considerable interest. The present work was carried out with the purpose of discovering effective catalysts for solid phase polyamidation in order to shorten the process.

As a result of studies concerning the catalytic action of various additions on the polycondensation of aminoenanthic acid in the solid phase, many substances of acidic, basic and neutral nature were found capable of accelerating the process. Of the 11 additions employed, the most effective catalyst was found to be boric acid in an amount equal to 1 per cent per weight of the aminoenanthic acid. The use of boric acid makes it possible to shorten considerably the solid phase polycondensation of aminoenanthic acid to form a polyenanthamide giving solutions of sufficient viscosity for the formation of stable fibres.

CARBOCHAIN POLYMERS AND COPOLYMERS—XIX. THE INTERACTION OF POLYMETHYLMETHACRYLATE AND POLYETHYLENESEBACATE

H. S. Kolesnikov, Tsen Khan'-Min, Vysokomol. soedin. **1**: No. 11, 1733–1738, 1959.

THE effect of the ratio of polyethylenesebacate and polymethylmethacrylate on the yield and properties of the graft copolymer formed has been investigated. The fall in the intrinsic viscosity observed with increasing degree of grafting has been shown not to be the result of degradation of the polymethylmethacrylate chain, the graft copolymer being converted to the original polymethylmethacrylate by methanolysis in the presence of hydrochloric acid.

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ABSTRACTS FROM PAPERS PUBLISHED IN *VYSOKOMOLEKULIARNYE SOEDINENIIA* Vol. 1, No. 12, 1959*

INFRA-RED SPECTROSCOPIC STUDIES OF THE AGING OF POLYVINYLETHYLAL

E. V. Shuvalova, Vysokomol. soedin. **1**: No. 12, 1749–1753, 1959.

ABSORPTION spectra in the ranges 2 to 15 μ and 220 to 600 mμ have been obtained of polyvinylethylal films subjected to heat treatment at 150°C or ultra-violet irradiation (photo aging) in the presence of air. For both kinds of aging a decrease in the number of $-C-O-$, CH and OH groups and the appearance of $C=C-O-$ groups (1730 and 1240 cm^{-1}) have been noted. In addition $C=C$ groups (1650 cm^{-1}) appear accompanied by yellowing of the specimens during the thermal aging.

COPOLYMERIZATION OF VINYL ACETATE AND CROTONAMIDE OR METHYLOLCROTONAMIDE

S. N. Ushakov, L. B. Trukhmanova, Vysokomol. soedin. **1**: No. 12, 1754–1757, 1959.

A STUDY has been made of the copolymerization of vinyl acetate and crotonamide or methylolcrotonimide. The copolymerization constants of the systems have been calculated (by the selected curve method). For the system crotonamide-vinyl acetate $r_1 = 0{\cdot}01 \pm 0{\cdot}01$ and $r_2 = 2{\cdot}0 \pm 0{\cdot}5$; for methylolcrotonamide-vinylacetate $r_1 = 0{\cdot}01 \pm 0{\cdot}01$ and $r_2 = 0{\cdot}045 \pm 0{\cdot}1$. The relative activity of crotonic acid and methylolcrotonamide towards the vinyl acetate radical has been found to be of the same order, whereas for the crotonamide monomer it has been found to be lower. The relative activities of the vinyl acetate monomer towards radicals of crotonic acid and its amide and of methylolcrotonamide are all equal.

MIXED POLY-4-AMINO-1,2,4-TRIAZOLES

V. V. Korshak, G. N. Chelnokova, M. A. Shkolina, Vysokomol. soedin. **1**: No. 12, 1772–1777, 1959.

MIXED poly-4-amino-1,2-4-triazoles have been synthesized and investigated. The investigation involved the following systems: (1)sebacic, adipic acids-hydrazine; sebacic, azelaic acids-hydrazine; azelaic, adipic acids-hydrazine; azelaic, adipic, sebacic acids-hydrazine.

It has been shown that incorporation of the second and third compounds into the polymer chain lowers the structural regularity of the latter and diminishes the cohesion forces of the macromolecules. In comparison with pure polymethylene-4-amino-2,2,4-triazoles the mixed products possess a lower melting temperature and greater solubility in organic solvents.

It was found in the study that exchange reactions do not take place in the polycondensation of hydrazine with dicarboxylic acids at a 2:1 ratio of the reagents.

* English abstracts reprinted from Vysokomol. soedin. **1**: No. 12, 1959.

ON THE WELDING OF RIGID THERMOPLASTIC HIGH POLYMERS—I. THE EFFECT OF WELDING CONDITIONS ON THE WELDING PROCESS

N. A. Grishin, S. S. Voyutskii, Vysokomol. soedin. **1**: No. 12, 1778–1787, 1959.

A STUDY has been made on the effect of welding conditions on the parting force of welded polymers. The strength of the weld has been shown to increase with increase in the pressure and the duration of the welding process, approaching a given limit. This bears evidence of the diffusion character of the process. The weld strength increases with the welding temperature. In the case of polar polymers the curve: weld strength–welding temperature possesses two plateaus: the first lying within the high elastic range corresponds to segment diffusion, whereas the second lying within the range of viscous flow corresponds to diffusion of the entire molecule. It has been found that additional heat treatment of welded polymethylmethacrylate may increase its strength owing to additional diffusion of the macromolecular segments, but at times as a result of rediffusion the strength may be reduced.

ON THE WELDING OF RIGID THERMOPLASTIC HIGH POLYMERS—II. EFFECT OF THE POLYMER PROPERTIES ON THE WELD

N. A. Grishin, S. S. Voyutskii, Vysokomol. soedin. **1**: No. 12, 1788–1794, 1959.

IT has been shown that with increase in the polarity of organic glasses their welding strength decreases owing to impairment of self-diffusion of the polymer chains. In general the strength of the weld has been found to increase with increasing plasticizer content evidently owing to facilitation of the selfdiffusion of the macromolecules and their segments. On welding in the high elasticity temperature range the macromolecules are oriented perpendicularly to the plane of the welding seam which leads to considerable fall in strength of the latter because of the hinderance of self-diffusion of the macromolecular segments in the direction of the orientation.

THE STRUCTURE OF 1, n-HEXAMETHYLACETOXYMETHYLMETHYLSILOXANE AND THEIR PHYSICAL PROPERTIES

K. A. Andrianov, G. E. Golubkov, Vysokomol. soedin. **1**: No. 12, 1801–1804 1959.

THE effect of the acetomethyl ester group on the physical properties of linear 1,*n*-hexamethylacetoxymethylmethylsiloxanes and of the cyclic triacetoxymethyltrimethylcyclotrisiloxane has been investigated and it has been found that the dipole moments and the dielectric constant increase with increasing number of silicon atoms in the molecule.

The values of the dielectric constant and of the dipole moments of 1,*n*-hexamethylacetoxymethylmethylsiloxanes are above those of compounds with similar structure containing a phenyl, chlorophenyl or phenylaminomethyl group in place of the acetate group.

Triacetoxytrimethylcyclotrisiloxanes posses the highest values of the dielectric constants and high dipole moments, indicating an asymmetric location of the acetoxymethyl groups in the cycle.

ELECTRON MICROSCOPIC STUDY OF STRUCTURES ARISING DURING INTERACTION OF POLYELECTROLYTE MACROMOLECULES

N. F. Bakeev, V. S. Pshezhetskii, V. A. Kargin, Vysokomol. soedin. **1**: No. 12, 1812–1816, 1959.

MIXTURES of polyelectrolytes of various strengths have shown that the shape of the structures formed on interaction of polybases depends upon the strength of the latter.

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Thus on interaction of strong polyelectrolytes (polydimethylpropylammonium oxide with its acrylic and ethylenesulfo acid copolymers) loose structures are formed of irregular shape and varying dimensions. The interaction of weak polyelectrolytes (polyacrylic acid and polyvinylpyrollidone) leads to the formation of compact structures characterized by regular shapes.

POLYMERS WITH CONJUGATED BONDS IN THE MACROMOLECULAR CHAINS – V. SYNTHESIS AND SOME PROPERTIES OF POLYARYLVINYLENES

A. A. Berlin, M. I. Cherkashin, O. G. Selskaia, V. E. Limanov, Vysokomol. soedin. **1**: No. 12, 1817–1820, 1959.

A STUDY has been made of the thermal polymerization of phenylacetylene and *p*-diethynylbenzene and of the copolymerization of phenylacetylene and polyphenylvinylene with *p*-diethynylbenzene. It has been shown that at 150–400° dark coloured polymers are formed with enhanced thermal stability.

The formation of higher molecular weight polyphenylvinylenes at 300–400° gives grounds to the belief that polymerization of compounds of the acetylene series differs from that of a radical mechanism. It is highly propable that the process proceeds through the formation of stable radicalides.

Polymerization of phenylacetylene with the formation of soluble and fusible polymers may take place at 70° also in the presence of a Ziegler catalyst.

A STUDY OF THE DIPOLE POLARIZATION OF *p*-CHLOROSTYRENE–ISOPRENE AND *p*-CHLOROSTYRENE–STYRENE COPOLYMERS

G. P. Mikhailov, L. L. Burshtein, Vysokomol. soedin. **1**: No. 12, 1824–1829, 1959.

IN the report a study has been made of molecular interaction of *p*-chlorostyrene-styrene and of *p*-chlorostyrene–isoprene copolymers by means of dielectric polarization method.

Based on the relation found between the correlation parameters and the concentration as attempt has been made to establish a connexion between the effective dipole moment and the time dipole-elastic relaxation.

A STUDY OF THE INTERACTION BETWEEN *ISO*PROPYLBENZENE HYDROPEROXIDE AND RONGALITE AND THE USE OF THE REACTION TO INITIATE POLYMERIZATION IN ACID MEDIA

B. E. Kutsenok, E. I. Tiniakova, B. A. Dolgoplosk, Vysokomol. soedin. **1**: No. 12, 1830–1839, 1959.

THIS investigation has been devoted to a study of the mechanism underlying the action of an oxido-reduction system with the participation of rongalite and of the use of the system for initiating polymerization in acid media with the purpose of obtaining carboxylated polymers. Determinations were made of the kinetics of interaction between rongalite and *iso*propylbenzene hydroperoxide in aqueous solutions of varying pH and of the composition of the products.

It has been shown that the system rongalite-hydroperoxide may be used in the absence of iron salts to initiate polymerization in acid media at 30–50°. Under such conditions the initiation is due to direct interaction between the hydroperoxide and rongalite.

It has been shown that iron salts in negligible quantities accelerate the interaction between hydroperoxide and rongalite, owing to which the system may be employed as initiator of acidic polymerization at lower temperatures. In the system the part played by rongalite is to reduce Fe^{3+} to Fe^{2+}.

AUTOMATIC APPARATUS FOR THE TURBIDIMETRIC TITRATION OF POLYMER SOLUTIONS

V. V. Guzeev, V. I. Morozov, B. P. Shtarkman, E. E. Rytov, Vysokomol. soedin. **1**: No. 12, 1840–1843, 1959.

An automatic apparatus has been devised for the turbidimetric titration of polymer solutions that may be employed both for determining the molecular weight distribution of the polymers (with preliminary plotting of nomograms by means of a few rather narrow fractions) as well as for the qualitative analysis of the polymers.

With the purpose of eliminating errors introduced by the heat effects during dilution and precipitation of suspensions, internal thermo-control was applied in the cell using a thermistor.

In calculating the turbidimetric density account was made of the volume effects in the mixing of the precipitant and solvent.

THE USE OF ALUMINOORGANIC COMPOUNDS AS CATALYSTS OF THE POLYMERIZATION OF 3,3′-*BIS*-(CHLOROMETHYL)-OXA*CYCLO*BUTANE AND *ISO*BUTYLENE

V. A. Kropachev, B. A. Dolgoplosk, N. M. Geller, Ia. M. Rosenoer, Vysokomol. soedin. **1**: No. 12, 1844–1847, 1959.

It has been shown that aluminum ethyldichloride may be used as cationic catalyst in the polymerization of 3,3′-*bis*-(chloromethyl)-oxa*cyclo*butane and *iso*butylene. It has furthermore been found that diethylaluminumchloride and triethylaluminum also bring about the polymerization of 3,3′-*bis*-(chloromethyl)-oxa*cyclo*butane, in this case polymers with high intrinsic viscosity (up to 1·23) being formed.

STUDIES ON THE SPHERULITE STRUCTURE OF POLYMERS—I. DEGRADATION OF POLYMER SPHERULITES UNDER THE ACTION OF FAST ELECTRONS

P. V. Kozlov, Li Pan-Tun, N. F. Bakeev, Vysokomol. soedin. **1**: No. 12, 1848–1852, 1959.

A study has been made of the action of fast electrons on the spherulite structure of polyethylene, polypropylene and polyethylenesebacate.

It has been shown that in the course of irradiation amorphization of the specimens first sets in, followed by degradation of the spherulite structure, causing the disappearance of the Maltese Cross on examining the specimens in a polarization microscope with crossed nicols. The topographic picture of the spherulites observed in the electron microscope remains unchanged throughout all stages of irradiation.

The degradation temperature of the internal structure of the spherulites irradiated with fast electrons has been found to be the higher the greater the irradiation dose of the specimens.

ON SOME METHODS OF SYNTHESIS OF GRAFT POLYMERS

N. A. Plate, V. P. Shibaev, V. A. Kargin, Vysokomol. soedin. **1**: No. 12, 1853–1858, 1959.

The treatment of polyacrylic acid and polyvinyl alcohol with ozone with the object of forming on them active peroxide groups and of the subsequent polymerization of styrene did not lead to successful synthesis of graft polymers, because the polyacrylic acid was too unstable and the polyvinyl alcohol too stable towards the action of ozone.

Polyacrylic acid-styrene and polyvinyl alcohol-styrene copolymers have been obtained mechano-chemically with the aid of a newly devised laboratory screw masticator. The solubility of such systems with varying proportion of components is intermediate between the solubilities of the polymer components.

ON THE SYNTHESIS OF THERMOREACTIVE COPOLYMERS OF METHYLOLCROTONAMIDE AND VINYL ALCOHOL OR VINYL ACETATE

S. N. Ushakov, E. M. Lavrent'eva, Vysokomol. soedin. **1**: No. 12, 1862–1867, 1959.

VINYL acetate-methylolcrotanamide copolymers were synthesized by copolymerization of different proportions of the monomer mixtures both in block and in methyl alcohol solution in the presence of benzoyl or acetylbenzoyl peroxides. The copolymers were transformed to vinyl alcoho l-methylcrotanamide copolymers by methanolysis in the presence of KOH (2·7-5% therotical). Both types of copolymers possess thermoreactive properties and pass over to the non-melting and insoluble state on heating, an increase taking place in the time-tensile strength value. Formation of tri-dimentional polymers during thermal treatment is due to reaction between the N-methylol groups of adjacent macromolecular chains with the formation of ether or methylene linkages, depending upon the conditions of the treatment.

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PAPERS FROM *VYSOKOMOLEKULIARNYE SOEDINENIIA* TO BE PUBLISHED IN FULL IN FUTURE ISSUES OF POLYMER SCIENCE: U.S.S.R.

V. S. Ivanov, M. A. Sokolova, S. V. Aver'ianov, V. F. Yevdokimov and I. S. Gurliand: Radiation polymerization of isoprene.—I

V. N. Tsvetkov and S. Ia. Lyubina: Volume effects and asymmetry of macromolecular chains in solution

M. A. Mokul'skii: Kinetic processes in irradiated substances

S. E. Bresler, A. T. Os'minskaia and A. G. Popov: The thermal degradation of stereoregular polypropylene

V. A. Kargin, V. A. Kabanov and T. K. Metel'skaia: Polymerization on a potassium-carbon black catalyst

Z. V. Popova and D. M. Yanovskii: The stabilization of polyvinylchloride by autocondensation products of cyclohexanone

B. A. Dogadkin, I. Mladenov and I. A. Tumorskii: Reactions of carboxylated butadiene-styrene rubbers under the action of γ-radiation

B. E. Eskin and O. Z. Korotkina: The light scattering and viscosity of solutions of poly-β-vinylnaphthalene in an ideal solvent

K. A. Andrianov and G. E. Golubkov: Polydimethylpolyphenylsiloxanes by catalytic condensation

V. A. Kargin, V. A. Kabanov and V. P. Zubov: The production of isotactic polymethylmethacrylate by polymerization of the frozen monomer

Iu. L. Spirin, A. R. Gantmakher and S. S. Medvedev: Ultraviolet absorption spectra of carbanions in the polymerization of styrene in the presence of organometallic compounds

G. V. Vinogradov and V. N. Manin: The rheological properties of concentrated polymer solutions

V. I. Anosov and A. A. Korotkov: The low temperature copolymerization of isobutylene with small amounts of diene hydrocarbons in the presence of boron trifluoride

A. A. Korotkov and N. N. Chesnokova: Catalytic copolymerization of styrene and butadiene

G. A. Razuvaev, K. S. Minsker, G. T. Fedoseeva and V. K. Bykhovskii: The effect of polar additives on the stereospecific polymerization of propylene

K. A. Petrov, E. E. Nifant'ev and L. V. Fedorchuk: Polymers containing phosphorus—I. Synthesis and polymerization of ethylenealkylphosphates

L. Kiss and Ia. Dobo: Graft copolymerization of methyl methacrylate and styrene on to gelatin induced by ionizing radiation

S. G. Entelis, V. Ia. Shliapintokh, O. N. Karpukhin and O. V. Nesterov: Chemiluminescence in the solvent and phase boundary production of nylon

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RADIATION POLYMERIZATION OF ISOPRENE—I*

V. S. IVANOV, M. A. SOKOLOVA, S. V. AVER'IANOV, V. F. YEVDOKIMOV and I. S. GURLIAND

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(*Received* 7 *July* 1959)

THE question of the radiation polymerization of isoprene is of interest from the points of view of the use of a new method of polymerization and of an examination of the possibility of making a polymer of isoprene closely similar in properties to natural rubber.

The polymerization of isoprene by α-rays from radon was first observed by Heising [1], but the products were not investigated. Burlant and Green [2] have presented, in a short communication, the results of a study of the effect of the polymerization mechanism on the molecular structure of synthetic polyisoprenes. In addition to samples of polyisoprene obtained by the usual methods of radical and ionic polymerization the authors studied polyisoprenes produced by γ-rays from a ^{60}Co source at $-40°$ and $+20°$. The content of segments of different structures was determined by infra-red spectroscopy. Up to the present time there has been no systematic study of the radiation polymerization of isoprene.

The aim of the present work was to obtain preliminary data on the effect of the conditions of irradiation of isoprene (dosage, intensity, addition of CCl_4) on the yield, molecular weight and molecular structure of the polymer. The radiation conditions, the results of the measurements and the G-values calculated from these are given in Table 1.

These figures show that the yield of polyisoprene is proportional to the irradiation dosage within narrow limits of variation of intensity (experiments 2–7). Comparison of experiments 1 and 2 shows that the yield increases with a decrease in intensity.

The order of magnitude of the mean molecular weights does not depend on the dosage within the limits of experimental error. The mean molecular weight of the polymer increases with a decrease in intensity of irradiation.

It is interesting to note that the addition of 5 moles per cent of CCl_4 as sensitizer increases the yield of polymer by a factor of approximately 2 and has no effect on its mean molecular weight or molecular structure.

It is important to note that the ratio of the elements of molecular structure of the polyisoprene (1,2; 3,4 and 1,4 segments) is practically independent of the

* Vysokomol. soedin. **2**: No. 1, 35–37, 1960.

TABLE 1. RADIATION POLYMERIZATION OF ISOPRENE BY γ-RAYS FROM A ^{60}Co SOURCE

Experiment No.	Dosage (mr)	Intensity (r/hr × 10^{-3})	Yield of polymer (weight %)	G-value (molecules /100 ev)	Viscosity average molecular weight × 10^{-3}	Content of segments (%)		
						1·2	3·4	1·4
1	1·0	1·3	2·4	268	75·0	6·8	7·3	85·9
2	1·0	510	1·0	113	—	—	—	—
3	12·3	720	3·0	26·8	8·0	7·3	8·1	84·6
4	31·5	720	7·8	27·8	6·4	6·7	8·3	85·0
5	83·3	720	14·9	20·2	4·2	7·5	8·9	83·6
6	163·7	380	30·1	20·7	8·0	8·9	10·0	81·1
7*	81·2	350	33·0	46·0	3·8	6·8	8·0	85·2
Burlant and Green [2]	10·0	—	conversion 1%	—	—	8·0	8·0	84·0

* 5 moles % of CCl_3 was added to the isoprene.

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radiation dosage and intensity, and of the presence of sensitizer. The conformity of these results with others in the literature [2] indicates that the molecular structure of radiation polyisoprene is also independent of other features of the experimental method within the temperature interval from −40° to +20°.

EXPERIMENTAL

Starting materials. Isoprene (redistilled) was redistilled over metallic sodium through a fractionating column, in a current of dry nitrogen. B.p. 33·8–33·9°; d_4^{20} 0·6808; n_D^{20} 1·4205. According to the literature, b.p. 34·07°; d_4^{20} 0·6805; n_D^{20} 1·4216 [3].

The isoprene content of the product obtained, determined by reaction with maleic anhydride, was 99·8 per cent.

Sources and radiation regime. Irradiation was carried out in a GUT-400 unit (142 g-equiv of radium) in experiment 1 and in a K-1400 unit (1400 g-equiv of radium) in experiments 2–7, at room temperature in an atmosphere of nitrogen in sealed, glass ampoules. Sample weight, 6–12 g.

Isolation of the polymer from its solution in the monomer was effected by distilling off the isoprene, at first under water-pump vacuum (10–11 mm) and then at 1 mm pressure (oil-pump), to constant weight of the residue. The yield of polymer in relation to dosage and intensity of irradiation was determined, precautions being taken against oxidation of the polyisoprene by oxygen of the air. The product was a colourless, transparent, very viscous mass.

Polymer characteristics. The mean molecular weight and content of the 1,2; 3,4 and 1,4 structural units of the polyisoprene obtained were determined.

The viscometric method was used for the determination of molecular weight. The viscosity of solutions of the polymer in toluene was measured in an Ostwald viscometer and the molecular weight was calculated from the equation

$$\log \overline{M} = 4{\cdot}946 + 1{\cdot}5 \log [\eta]$$

The molecular structure was studied by infra-red spectroscopy. The absorption spectra of the polyisoprene samples were recorded in an IKS-6 spectrometer with an NaCl prism, in solution in a liquid cell. The spectra were plotted over the range 850–950 cm^{-1}. The absorption band corresponding to 1,4 *cis* and *trans* segments (840 cm^{-1}) could not be obtained because carbon tetrachloride was used as solvent and this absorbs completely in the 800–840 cm^{-1} region. The content of 1,4 segments (sum of *cis* and *trans*) was found by difference from percentage contents of 1,2 and 3,4 segments (absorption maxima 910 and 888 cm^{-1} respectively). For finding the absorption coefficients at the maxima 1-pentene (1,2 segment model) and 2-methylbutene-1 (3,4 segment model) were taken. Comparison with data in the literature [4] indicates that the absorption coefficient at the maximum, α_{max}, for the 910 and 888 cm^{-1} bands may be taken as 137 cm. moles (precision 8 per cent) and 154 cm. moles (precision 3 per cent) respectively.

We are grateful to G. S. Denisov for valuable advice and assistance in the plotting of the infra-red spectra.

CONCLUSIONS

(1) The irradiation of isoprene with γ-rays from a ^{60}Co source gives a polymer, the yield of which is directly proportional to the irradiation dosage within narrow limits of variation of intensity.

(2) The molecular structure of the polymer obtained is independent of the dosage and intensity of irradiation and of the presence of a sensitizer.

(3) The mean molecular weight of the polyisoprene increases with decreasing intensity of irradiation.

Translated by E. O. PHILLIPS

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VOLUME EFFECTS AND ASYMMETRY OF MACROMOLECULAR CHAINS IN SOLUTION*†

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(*Received* 24 *September* 1959)

IN an earlier paper [1] the influence of volume effects (long range interaction) on the segmental anisotropy of linear, polymeric chains in solution was examined.

A study of streaming birefringence in the absence of shape effects has shown that an increase in the dimensions of the molecular cluster, brought about by long range interaction effects, leads to an increase in the intrinsic birefringence $[n]$ proportional to the increase in the intrinsic viscosity of the solution $[\eta]$. The constant value of $[n]/[\eta]$ indicates that volume effects do not effect the segmental anisotropy of the cluster. It must therefore be considered that the size and number of segments in the molecule do not change with the increase in dimensions of the molecular chain in a good solvent. On the other hand the distribution of the segments in the macromolecule undergoes change in these circumstances, becoming non-Gaussian.

Such a change in the segmental statistics of the cluster can in principle lead to a change in its shape because the asymmetry of the latter is different for Gaussian [2] and non-Gaussian mass distributions.

In the present work the effect on the shape of the molecular chain is studied by the method of streaming birefringence in a polymer-solvent system in which segmental anisotropy plays a negligibly small part in comparison with the shape effect [4] in the observed anisotropy of the solution.

MATERIAL STUDIED AND METHOD

The temperature dependence of viscosity and birefringence of three fractions of polybutylmethacrylate (PBMA) in isopropanol was investigated in this work. These same fractions in ethyl acetate have been studied previously [5]. The molecular weight, M, of the fractions was determined viscometrically in methyl-

* Vysokomol. soedin. **2**: No. 1, 75–81, 1960.

† *Translator's note*: The problem of terminology is rather difficult in this paper, e. g. the correct rendering of "characteristic double refraction of form"—given in this translation as "intrinsic shape-effect birefringence". I had hoped to obtain some guidance from Frisman and Tsvetkov's paper in J. Polymer Sci. (**30**: 297, 1958), but there appears to have been little or no attempt to arrive at any consistent solution of the problem in that translation.

ethylketone, using Chinai's equation [6]. The molecular weights found for these three fractions were $6{\cdot}4\times10^6$; $2{\cdot}2\times10^6$; and 2×10^5 respectively.

It is known that isopropyl alcohol at 21·5° is an ideal solvent for PBMA. Hence measurements of the viscosity and optical anisotropy of the solutions were made in the temperature region from Flory's θ-point (21·5°) to 45°C.

The viscosity measurements were carried out in an ordinary capillary viscometer with an efflux time for isopropanol of 70·2 sec at 21·5°C.

The birefringence of the solutions was studied by means of a "dynamo-optimeter" with an external rotor [7] in the apparatus used previously [5]. Since the refractive index of isopropyl alcohol, used as solvent ($n_s=1{\cdot}377$ at 21·5°), is much less than that of PBMA ($n_k=1{\cdot}50$), the observed birefringence of the solutions is determined to a considerable extent by the shape effect [4].

RESULTS

Figure 1 shows the dependence of reduced viscosity, $[\eta]_1=\eta_{sp}/C$, on concentration C, for the second PBMA fraction ($M=2{\cdot}2\times10^6$) at various temperatures (from 19·5° to 45°C).

Similar dependences were obtained also for the other two fractions (I and III).

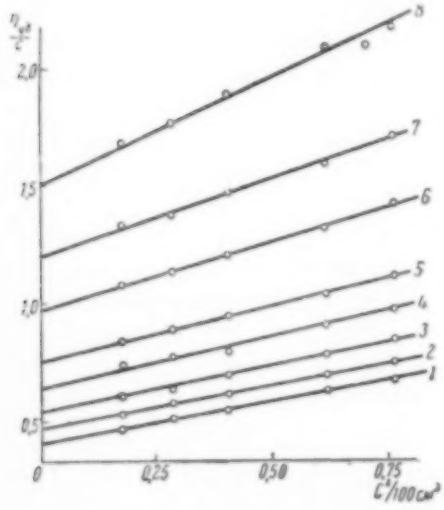

FIG. 1. Dependence of reduced viscosity η_{sp}/C on concentration at various temperatures (in °C) for PBMA in isopropanol. Fraction II. (1) 19·5, (2) 20·5, (3) 21·5, (4) 23, (5) 25, (6) 30, (7) 35, (8) 45°C.

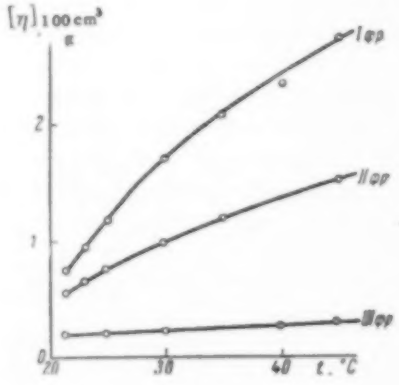

FIG. 2. Temperature dependence of intrinsic viscosity, $[\eta]$, of PBMA fractions in isopropanol.

All the points as usual lie on straight lines, the extrapolation of which to $C\to0$ gives the intrinsic viscosities shown in the third column of the table. The

values of the Huggins constant K', calculated from the slope of the lines $\eta_{sp}/C = f(C)$, are given in the fourth column of Table 1. The values of K', as usual, decrease rapidly with increasing temperature i.e. with increase in the solvating power of the solvent.

On the other hand the intrinsic viscosity, $[\eta]$, increases with increasing temperature, i.e. with increase in the solvating power of the solvent and corresponding uncoiling of the polymer chains. The temperature dependence of $[\eta]$ is shown graphically in Fig. 2.

It should be borne in mind that in passing from a poor to a good solvent the constant Φ in Flory's equation

$$[\eta] = \Phi \frac{(h^2)^{3/2}}{M} \tag{1}$$

decreases.

Consequently the mean square length of the chain $(h^2)^{1/2}$ increases more rapidly than $[\eta]^{1/3}$ in these circumstances. For example for fraction I in the temperature interval from 21° to 45° the statistical length $(h^2)^{1/2}$ increases by a factor of 1·9.

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Measurement of the streaming birefringence, Δn, of the solutions gave the following results.

For all the solutions over the whole range of velocity gradients, g, investigated (from 0 to 3000 sec^{-1}), Δn was positive and increased proportionally with g. The slope $\Delta n/g$ of the straight line $\Delta n = f(g)$ decreased with increasing temperature for a given solution.

As an example, the temperature dependence of $\Delta n/g$ of solutions of fraction II at various concentrations, is shown in Fig. 3.

By making use of the experimental curves $\Delta n/g = f(C)$ and the viscosity of the solvent η_0 the values of the reduced birefringence $[n]^* = \Delta n/g\eta_0 C$ can be obtained for different concentrations and temperatures. The results obtained are shown graphically in Fig. 4, 5 and 6, which give the concentration dependence of $\Delta n/g\eta_0 C$ at various temperatures for the three fractions examined.

The curves of the relationship $[n]^* = f(C)$ are complex in shape, quite different from that of the curves of $[\eta]^* = f(C)$ given in Fig. 1.

For the low-molecular fraction (Fig. 4) at high temperatures the concentration dependence is slight, however as the temperature decreases it becomes more definite and close to the θ-point it is very marked. Over the whole range of temperatures and concentrations it is positive ($[n]^*$ increases with concentration).

For the high-molecular fractions (Fig. 5 and 6) in the low concentration region the concentration dependence of $[n]^*$ is negative ($[n]^*$ decreases with increasing C) and is more pronounced the higher the temperature. With increasing concentration the concentration dependence changes sign, becoming positive, and with the change in sign the increase in $[n]^*$ with increasing C is more pro-

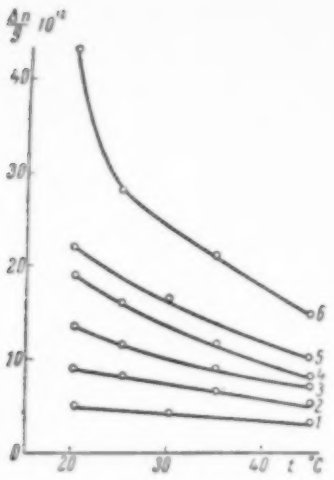

FIG. 3. Temperature dependence of streaming birefringence, $\Delta n/g$, of solutions of PBMA fraction II ($M = 2{\cdot}2 \times 10^6$), in isopropanol at various concentrations, C (per cent) (1) 0·1, (2) 0·2, (3) 0·303, (4) 0·43, (5) 0·5, (6) 0·76 per cent.

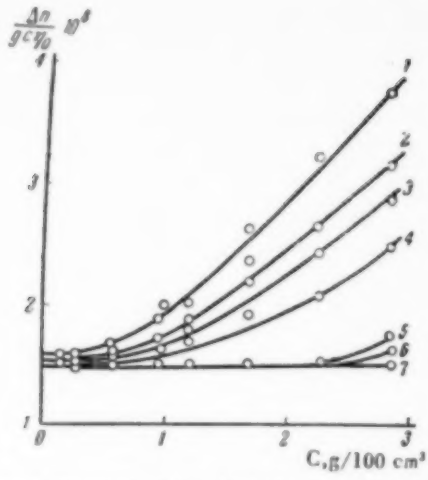

FIG. 4. Concentration dependence of reduced birefringence, $\Delta n/gc\eta_0$, of solutions of fraction III ($M = 2 \times 10^5$) at various temperatures (°C) (1) 21, (2) 22, (3) 23, (4) 25, (5) 30, (6) 31, (7) 52°.

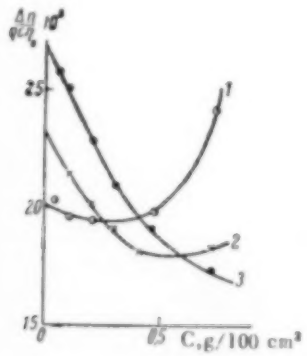

FIG. 5. Concentration dependence of reduced birefringence, $\Delta n/gc\eta_0$, of solutions of fraction II ($M = 2{\cdot}2 \times 10^6$) at various temperatures (°C) (1) 26, (2) 30, (3) 45°.

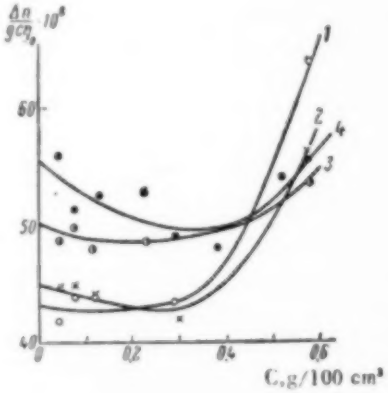

FIG. 6. Concentration dependence of reduced birefringence, $\Delta n/gc\eta_0$, of fraction I ($M = 6{\cdot}4 \times 10^6$) at various temperatures (°C) (1) 21·5, (2) 25, (3) 30, (4) 41°.

nounced the lower the solution temperature. Consequently the curves of $[n]^* = f(C)$ for the high-molecular fractions at different temperatures intersect one another.

Extrapolation of the curves (Fig. 4, 5 and 6) to $C \to 0$ gives the intrinsic birefringence, $[n] = \lim_{C \to 0} [n]^*$, at the given temperature. The values of $[n]$, obtained

TABLE 1. VALUES OF THE INTRINSIC VISCOSITY AND BIREFRINGENCE OF PBMA FRACTIONS IN ISOPROPANOL AT VARIOUS TEMPERATURES

Fraction No.	Temperature (°C)	$[\eta]\times10^{-2}$ (cm³/g)	K'	$[n]\times10^{8}$	$-[n]_e\times10^{8}$	$[n]_f\times10^{8}$	P
Fract. I; M = $6{\cdot}4\times10^{6}$	45	2·72	0·703	52	3	55	2·06
	40	2·30	0·907	—	2·5	—	—
	35	2·03	0·947	—	2·3	—	—
	30	1·68	1·13	48	1·85	50	2·00
	25	1·17	1·53	44	1·3	45	1·95
	23	0·96	2·17	—	1·1	—	—
	21·5	0·74	3·65	43	0·81	44	1·90
Fract. II; M = $2{\cdot}2\times10^{6}$	45	1·51	0·40	25·5	1·6	27	2·30
	35	1·20	0·46	—	1·3	—	—
	30	0·98	0·62	23	1·1	24	2·20
	25	0·76	0·77	21·5	0·81	22	2·15
	23	0·65	1·01	—	0·71	—	—
	21·5	0·54	1·33	19·5	0·60	20	2·10
	20·5	0·47	1·62	—	—	—	—
	19·5	0·41	2·04	—	—	—	—
Fract. III; M = $2{\cdot}0\times10^{5}$	52	0·29	0·57	1·5	0·32	1·82	2·10
	41	0·23	0·93	1·5	0·25	1·75	—
	30	0·19	1·2	1·5	0·21	1·70	—
	25	0·174	1·06	1·5	0·19	1·69	2·00
	23	0·165	0·92	1·55	0·19	1·73	—
	22	0·158	0·86	1·55	0·17	1·72	—
	21	0·151	1·0	1·6	0·16	1·77	2·06

in this way, are given in column 5 of Table 1. For fraction III the value of $[n]$ is practically the same at all temperatures. For the high-molecular fractions (I and II) $[n]$ increases slightly with increasing temperature.

DISCUSSION

In the interpretation of these results the main point to be borne in mind is that the birefringence observed in the PBMA-isopropanol system is almost entirely an effect of shape [4].

For an infinitely dilute solution the fraction of the intrinsic birefringence contributed by the intrinsic anisotropy of the molecule, $[n]_e$, can be calculated from the known [5] segmental anisotropy of PBMA, $\alpha_1-\alpha_2$, according to Kuhn's theory [8]:

$$[n]_e=\frac{4\pi}{45}\,\frac{(n_s^2+2)^2}{KTn_s}\cdot[\eta]\cdot(\alpha_1-\alpha_2) \qquad (2)$$

By substituting in (2) the value of $\alpha_1-\alpha_2=-14\times10^{-25}$ cm^3, found by us previously [5], and using the values of $[\eta]$ from the third column of Table 1, we obtain the values of $[n]_e$ shown in column 6 of Table 1. Direct comparison of columns 5 and 6 shows that $[n]_e$ is only a small part of the observed effect $[n]$, which is the sum of $[n]_e$ and the shape effect $[n]_f$:

$$[n]=[n]_e+[n]_f \tag{3}$$

The values of $[n]_f$ calculated according to (3) from the data in columns 5 and 6, are given in column 7.

Since the observed birefringence is almost entirely a shape effect its concentration dependence in a good solvent must be analogous to that of the molecular anisotropy of shape, θ_f, the theory of which was developed in [9].

According to this theory, as a result of "optical interaction" of the molecular clusters the effective shape anisotropy of the cluster, θ_f^*, decreases with increasing concentration according to the equation

$$\theta_f^*=\theta_f(1-K[\eta]C+\ldots.) \tag{4}$$

where K is a positive constant and θ_f is the shape anisotropy of the cluster at infinite dilution.

Hence the decrease in reduced birefringence, $[n]^*$, with increasing concentration, observed in the high-molecular fractions in the low-concentration region (Fig. 5 and 6), can be explained, at least qualitatively, by means of equation (4). On the other hand the sharp increase in $[n]^*$ with concentration in the high-concentration region, observed in all the fractions, particularly at temperatures close to the θ-point (Fig. 4, 5 and 6), is obviously an effect opposed to optical interaction and cannot be explained by this.

We suggest that this phenomenon is of a totally different nature and is connected with the formation of molecular micro-aggregates in the solution at temperatures close to that at which the high-molecular and low-molecular components seperate out. It evidently bears some resemblance to the processes taking place in binary liquid mixtures which manifest themselves in anomalously large electrical birefringence [10] and anomalous light-scattering depolarization (the Krishnan effect) [11], close to the critical temperature of mixing of the components.

Naturally the phenomenon of aggregation is the more intensive the higher the concentration of the solution, as is observed experimentally.

Characteristically this aggregation has no effect on the viscosity of the solution in so far as the curves in Fig. 1 do not follow an anomalous course. This fact is readily explained because the formation of a negligibly small quantity of particles of "super-molecular" structure in the solution causes practically no change on its viscosity but can have a very marked effect on its dynamo-optical properties.

Figure 7 shows a graphical representation of the temperature dependence of the intrinsic shape-effect birefringence $[n]_f$ for the three fractions investigated. For the low-molecular fraction III the value of $[n]_f$ is almost unaffected by tem-

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perature. For fractions I and II it increases by 15–20 per cent with a rise of temperature of 30° above the θ-point. At the same time the intrinsic viscosities of the solutions increase a few times under the same conditions (Fig. 2). Thus the volume effects, while altering the dimensions of the molecular clusters in the so-

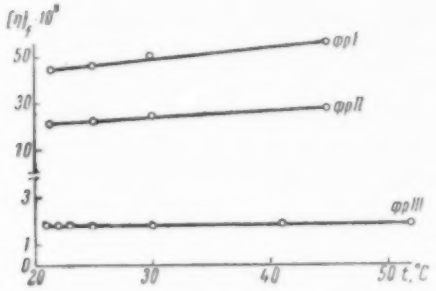

FIG. 7. Temperature dependence of intrinsic shape-effect birefringence, $[n]f$, for PBMA fractions in isopropanol.

lution and to the same extent increasing the intrinsic part of the birefringence $[n]_e$ [1], have little effect on the shape effect birefringence. For a quantitative consideration of this fact let us turn to the theory of the shape effect, according to which [4]

$$[n]_f = \frac{1}{120\pi\rho^2 RT} \cdot \frac{(n_k^2 - n_s^2)^2}{n_s^2} \cdot M \cdot f(P) \tag{5}$$

where ρ is the density of the dry polymer and $f(P)$ is a function of the ratio of the axes of the molecular ellipsoid, P.

The factor standing to the left of $f(P)$ in the right hand side of equation (5) can change little with an increase of temperature from 20° to 50°. Hence the small increase in $[n]_f$ observed for the high-molecular fractions with increasing temperature (see Table 1) can relate only to a corresponding increase in $f(P)$.

This increase is most marked in fractions I and II where it is about 25 per cent. But as the form of $f(P)$ indicates (see for example [12]) this increase in $f(P)$ corresponds to an increase in P of less than 10 per cent. The values of P calculated from equation (5) are given in the last colum of the table.

Thus the volume effects, while markedly increasing the dimensions of the molecular clusters in the solution, alter the asymmetry of their shape only very slightly.

The "swelling" of the molecular cluster, as a result of long-range interaction forces, takes place practically "isotropically" both in the sense of the invariability of the intrinsic (segmental) anisotropy [1] of the macromolecule and in relation to its geometric form.

CONCLUSIONS

The temperature dependence of the viscosity and streaming birefringence of three polybutylmethacrylate (PBMA) fractions in isopropanol, has been investigated.

It was found that an increase in the solvating power of the solvent (as a result of a change in temperature), resulting in an increase in the intrinsic viscosity of the solutions by a small factor, alters the value of the intrinsic birefringence only very slightly.

This result means that the volume effects (long-range), though markedly increasing the dimensions of the molecular chains in solution, have little effect on the asymmetry of the molecular clusters.

Translated by E. O. PHILLIPS

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KINETIC PROCESSES IN IRRADIATED SUBSTANCES*

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INTRODUCTION

IN recent years a number of papers have appeared, devoted to the study of the physical properties of substances subjected to high-energy radiation. The factors studied in these investigations are the macroscopic characteristics of the body—the mechanical relaxation properties [1–3], diffusion constant [4], electrical conductivity [5], optical properties (darkening) [6] etc. The effects observed in these investigations, often very great, depend considerably on the radiation intensity and disappear more or less rapidly after cessation of irradiation.

The basic experimental results of the study of the mechanical properties of high polymers during irradiation in a nuclear reactor are reported in references [1–3]. These results are as follows. In a radiation field the mechanical relaxation processes are strongly accelerated, e. g. creep and relaxation of stress at constant deformation, the limit of elasticity is lowered, etc. The effects of acceleration of the relaxation processes increase with increasing radiation intensity and disappear after irradiation ceases, hence they have been called reversible radiation-mechanical effects. It is known that covalent chemical bonds rupture under irradiation. In addition to investigation of the role of this phenomenon in the observed effects there is the need to consider whether there is not a non-chemical mechanism of acceleration of relaxation by irradiation, i. e. a mechanism not related to the rupture of chemical bonds.

A suggestion concerning the existence of such a mechanism has been put forward previously [1,3]. According to this suggestion the acceleration of the relaxation processes by irradiation is brought about by an increase in the concentration of "hot" molecules possessing an energy in excess of the energy of activation.

The present work is an attempt to develop a physical theory of the acceleration of kinetic processes by irradiation.

The effect of radiation on materials. The first stage in the action of radiation on a material consists in the ionization and excitation of the atoms of the substance by charged particles and γ-quanta and in the formation of recoil nuclei.

In the next stage recombination of ions and delocalization of excitation takes place. Defects resulting from the movement of atoms as a result of primary col-

* Vysokomol. soedin. **2**: No. 1, 119–129, 1960.

lisions are not of great significance in the case of materials with covalent bonds. In these materials the main part is played by processes resulting from excitation of the molecules.

The transition of a substance containing excited atoms and molecules to a state of thermodynamic equilibrium is brought about by the following three processes.

(1) The excitation energy is emitted in the form of photons (luminescence). Normally if the material has no luminophore the fraction of the energy turning to luminescence is very small.

(2) The excitation energy is expended in the rupture of chemical bonds and the formation of free radicals.

(3) The excitation energy of the molecules is converted directly into heat, i. e. the energy of the first, powerfully excited molecules (with an excitation energy of the order of tens of electron volts) is dispersed among a large number of particles. The last stage of this process is the heating of the body. In the last analysis it is on heating the material that the overwhelming part of the absorbed radiation energy is expended.

The energy liberated in chemical reactions of the free radicals is also converted to heat. Here again we have the stage of dispersal of strong excitations among a large number of particles.

It is clear that in principle, with a sufficiently large radiation intensity (in the absence of a marked temperature rise, as a result of good heat removal), the number of excited molecules in a body can be sufficiently large to enable their presence to be observed by changes in the macroscopic properties of the body. These changes will be apparent during the irradiation process and will disappear rapidly after irradiation ceases.

Estimation of the concentration of excited molecules and of the rate of the kinetic processes. It will be seen from what follows that at the radiation intensities at present attainable the stationary concentration of excited molecules is always very small. Consequently in practice reversible radiation effects can be sought only in those phenomena brought about by the presence in the material of a relatively small number of molecules possessing high energy. Of primary importance are all kinetic processes, i. e. processes requiring a certain activation energy for their accomplishment. These include relaxation of mechanical stress, diffusion, orientation of molecular dipoles in an electric field, many chemical reactions etc.

The temperature dependence of the rate of such processes (the rate is determined as the number of elementary acts per sec in 1 g of material) is expressed, as is known from the theory of absolute rate processes [7], by an equation of the type

$$n = N_0 \Omega e^{-U/kt} \tag{1}$$

in which the frequency factor Ω is also temperature dependent but not exponentially. N_0 is the number of molecules in 1 g of the substance. The exponential form of expression (1) is derived from the assumption that there is a

Boltzman energy distribution in the given kinetic process. However this condition is not fulfilled when the material is in a radiation field. The absorption of radiation creates in the material an anomalously high concentration of particles with energies much greater than the mean energy of thermal movement. The problem of finding the energy distribution in an irradiated material has not yet been solved. The main part of the absorbed radiation energy is dissipated in the material (as heat) in a time $\lesssim 10^{-13}$–10^{-10} sec [8]. The problem of the dissipation of energy in such a short time cannot be solved by the methods of statistical thermodynamics. The rate of a kinetic process in an irradiated material can be expressed by

$$n = N_0\Omega(T)w(U) = N_0\Omega(T)[w_B(U) + w_j(U)] \qquad (2)$$

Here $w(U)$ is the total probability of finding a particle with energy greater than U. When the material is in a radiation field $w(U)$ consists of two parts. Correspondingly $N_0 w_B(U)$ and $N_0 w_j(U)$ are the number of particles of energy greater than U as a result of the Boltzman energy distribution and as a result of the absorbed radiation energy. For definitiveness we shall consider the Boltzman distribution usually found, though in reality it can, of course, be otherwise. The magnitude of $w(U)$ must be normalized to unity by the condition $w(0)=1$; however, in practice because of the extraordinary smallness of $w_j(U)$ in comparison with unity this normalization condition can be replaced by $w_B(0)=1$.

We shall attempt to find some qualitative corollaries to equation (2). In this equation $w_B(U)$ is very strongly dependent on temperature (see equation (1)) and at $U \gg kT$ the value of $w_B(U)$ becomes very small. On the other hand it is natural to suppose that $w_j(U)$ will be little dependent on temperature. ($w_j(U)$ is deter-

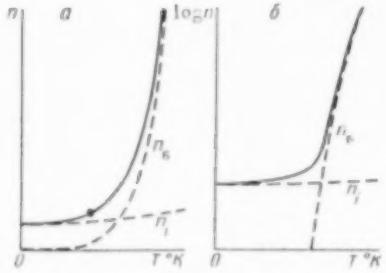

FIG. 1. The rate of a kinetic process in an irradiated material: (a) ordinary scale, (b) semilogarithmic scale.

mined by the radiation intensity and certain constants of the material that are much less temperature dependent than $w_B(U)$).

As a result of this, if the temperature is sufficiently low (the lower the temperature the lower the activation energy U) the value of $w_B(U)$ becomes lower than $w_j(U)$. Then the rate of the given process will be determined by the radiation intensity and will depend little on temperature.

The dependence of the rate of a kinetic process on temperature is depicted schematically in Fig. 1, a and b.

The dotted lines in the schematic graphs correspond to the "Boltzman" and "radiation" terms in equation (2); the continuous line is the overall rate.

In view of the fact that an exact expression for $w_j(U)$ was not obtained only an approximate estimation of this term can be made. For this estimation we shall use the hypotheses of the thermal conductivity theory. It is clear that the application of these hypotheses to the processes of delocalization of excitation taking place in a period of 10^{-13}–10^{-10} sec and involving a large number of particles ($\sim 10^3$) cannot give an exact result. It may be considered, however, that the values obtained will not differ from the true values by more than 1-2 orders (see below).

Let the radiation energy be transmitted to the particles of the medium in equal portions q and let there be formed c spherical regions of radius r_0 and energy q in 1 g of material per sec. Then $j=q.c$ ergs/g/sec. We are interested in the number of particles of the material possessing, under these conditions, energies greater then a cartain value of U.

After time t, as a result of thermal conductivity, the radius of a region containing particles with energy greater than U becomes equal to r when $t \sim r^2/\chi$ (χ is the thermal diffusivity of the medium) and $(r/r_0)^3 \sim q/U$.

Whence $t \sim (r_0^2/\chi)\,(q/U)^{2/3}$. The number of particles in such a region $m \sim q/U$. From the expression given it is evident that the stationary number of particles, $N_j(U)$, in 1 g of material, having an energy greater than U is

$$N_j(U) \sim cmt \sim c\,\frac{r_0^2}{\chi}\left(\frac{q}{U}\right)^{3/2} = j\,\frac{r_0^2}{\chi}\,\frac{q^{3/2}}{U^{3/2}}. \tag{3}$$

Hence

$$w_j(U) = \frac{N_j(U)}{N_0} \sim j\,\frac{r_0^2}{\chi N_0}\,\frac{q^{3/2}}{U^{3/2}}.$$

An exact solution of the problem* requires the introduction into the right hand side of equation (3) of a numerical factor of approximately 0.02.

Finally we shall give an expression for $w_j(U)$:

$$w_j(U) = 2 \times 10^{-2} j\,\frac{r_0^2 q^{3/2}}{\chi N_0 U^{3/2}}. \tag{4}$$

The condition for the applicability of equation (3) (within the framework of the thermal conductivity theory)—the absence of overlapping of heated regions, i. e. $w_j(U) \ll 1$—is fulfilled for any value of j attained.

For the case of the passage through the medium of high-speed electrons (from the Compton-or photo-effect, when there is primarily γ-radiation) it may

* An exact analytical solution of the problem of the distribution of temperature in a medium with δ-form heat sources was derived by I. M. Lifshits [9]. An equation similar to (3), in the form of an asymptotic expression, was obtained in reference [9]. The initial assumption was the same—that the constants of the medium are independent of temperature.

be taken that $q \sim 10$ ev and the dimensions of the region where this energy is initially liberated, $r_0 \sim 2 \times 10^{-8}$ cm (interatomic distance). Further, taking $\chi = 10^{-3}$ cm^{2}sec^{-1} and $N_0 = 10^{23}$ g^{-1} (for a substance of average atomic weight 6), we obtain

$$w_j(U) \approx 0{\cdot}5 \times 10^{-14} j U^{-5/2} \tag{5}$$

The maximal value of the radiation intensity j used in references [1, 2 and 3] was 5×10^6 ergs/g/sec. Taking the activation energy of a given process as $U = 1$ ev (23 kcal/mole) and substituting these values in (5), we obtain $w_j = 10^{-18}$ (independent of temperature). For the same value $U = 1$ ev we obtain $w_B(T \approx 310°\text{K}) \approx 10^{-16}$ and $w_B(T = 230°\text{K}) \approx 10^{-20}$.

In spite of the fact the equation (5) is essentially an estimation we can draw the following conclusion: a radiation intensity of 5×10^{-6} ergs/g/sec has slight effect on the rate of a process with an activation energy of 23 kcal/mole at a temperature of 310°K and above, on the other hand at 230°K and below the rate of this process is almost completely determined by the radiation. For a process with an activation energy of $U = 1{\cdot}3$ ev = 30 kcal/mole these temperatures become 410 and 300°K.

Let us now write expression (2) for the rate of a kinetic process in the following form:

$$v = N_0 \Omega(T) [w_B(U) + w_j(U)] = N_0 \Omega(T) [e^{-U/kT} + A j U^{-5/2}], \tag{6}$$

where

$$A = \frac{r_0^2}{\chi N_0} 2 \times 10^{-2} \cdot w^{-2} q^{3/2}.$$

A correct calculation of the process of delocalization of excitation energy would, of course, involve another expression for $w_j(U)$ but the basic features of this equation—a slight dependence of w_j on U and the existence of two regions of values of U/kT in one of which $w_j \ll w_B$ and in the other $w_j \ll w_B$—will be maintained.

An assessment of the minimal possible concentration of "hot" molecules in an irradiated material can be made as follows. Let us consider the process of delocalization of the primary excitation as a process of diffusion of energy. The maximal possible value of the diffusion constant of such a process is given by the expression $r_0 f$, where r_0 is the interatomic distance and f is the vibrational frequency of the atoms. (This expression is derived from the usual equation for the diffusion constant when the activation energy is taken as zero).

In the absence of electronic thermal conductivity it may be considered that this expression is equal to the coefficient of thermal diffusivity of the material, χ. The usual value for χ is obtained by substituting $r_0 = 2 \times 10^{-8}$ cm and $f \approx 10^{13}$ sec^{-1} (the frequency of thermal vibration). In the assessment of the time of delocalization of excitations with energies of the order of 1–10 ev it is necessary to take into consideration the fact that under these conditions f can have a considerably

higher value. Taking the value of f as $f \approx U/h$, where h is the Planck constant, we obtain $f \approx 3 \times 10^{14}$ at $U = 1$ ev and hence $\chi \approx 10^{-1}$. Obviously the true value of the coefficient χ at a "temperature" ~ 1 ev cannot be greater than 10^{-1}. For the estimation of the life of an excitation of 1 ev we took the value $\chi = 10^{-3}$. Thus if the calculated value of w_j (see (5)) exceeds the true value it does so by not more than some tens of times.

There is, however, a factor which, if taken into account, shows an increase in the effect of radiation on the rate of a kinetic process, in comparison with that indicated by equation (6). Strictly speaking, equations (2) and (6) should be written in the form.

$$n = N_0[\Omega_B w_B + \Omega_j w_j],$$

where Ω_B and Ω_j are frequency factors corresponding, in general, to different temperatures. Obviously Ω_j, being a frequency factor for a process taking place in a region heated by radiation, can be considerably graeter than Ω_B. The two factors not taken into account in equation (6)—the increase in thermal diffusivity and frequency factor with temperature—compensate for one another in order of magnitude. If it is considered that in a region heated by radiation to a temperature $T_j \sim U/k$, the thermal diffusivity $\chi \sim (U/h)r_0^2$ and the frequency factor $\Omega_j \sim kT_j/h \sim U/h$, then in place of equation (6) we obtain *:

$$n(U) = N_0 \frac{kT}{h} e^{-U/kT} + j2 \cdot w^{-3} q^{3/2} U^{-5/2}. \tag{7}$$

The numerical results obtained on the basis of this equation at ordinary temperatures are close to those obtained from equation (6). At lower temperatures a divergence appears. According to equation (6) the rate of a kinetic process approaches zero as $T \to 0$. The implication of equation (7), according to which under radiation conditions kinetic processes proceed at a finite rate at any temperature, however low, is more reasonable.†

For subsequent calculations and the construction of graphs we shall use equation (7). We shall retain the calculated coefficient 2×10^{-2} taken from [9], though it will, of course, be changed if the problem of the delocalization of energy in a material, taking into account the dependence of χ on T, is solved.

* It should be noted that the expression for the frequency factor kT/h, generally speaking, differs from the kT/h used by us, by a factor of the form $ae^{\Delta S/k}$, which is only slightly temperature dependent (see for example [7]). This factor can be close to unity but it can also have a totally different order of magnitude. It can be calculated for many concrete models. In subsequent expressions it will be taken as unity. This means that the absolute value of the rate of a kinetic process is calculated by us with a precision approximately equal to that of this factor (the factor can be different for the Boltzman and radiation terms of equation (7)).

† Equation (7) describes a simplified model. In a real case the two terms can differ considerably from those written, particularly at low temperatures.

Relaxation of mechanical stress. By taking the example of the relaxation of mechanical stress in a material subjected to irradiation it is possible to examine the main features of kinetic processes taking place under these conditions.

It is known that the relaxation of mechanical stress in a solid body is, from the molecular point of view, a successive rearrangement of particles of the material (for example, the segments of a polymeric molecule) leading to a reduction in stress or to the accumulation of nonelastic deformation. Every such act of rearrangement may be regarded as the transference of a particle through a certain potential barrier. The number of particles surmounting this barrier per sec depends on the height of the barrier U_1 and on the energy distribution of the particles.

We shall assume that it is determined by equation (7). The occurrence of n such transferences in 1 g of material brings about a reduction in stress of $\Delta\sigma = \sigma(n/N_0)$ (samples subjected to constant deformation are considered). Whence the reduction in stress in time dt is

$$d\sigma = -\sigma \frac{n(U_1)}{N_0} dt. \tag{8}$$

In the implications of this equation we have assumed, for simplicity, that the magnitude of all the barriers is U_1 and is independent of stress.

The effect of stress on the height of the barriers can, as is known, be accounted for approximately by introducing the relationship $U_1 = U_0 - \gamma\sigma$. Generalizing equation (8) to the case of an arbitrary dependence of deformation on time we obtain

$$\frac{d\sigma}{dt} = G\frac{d\varepsilon}{dt} - \sigma\frac{n(U_1)}{N_0} \tag{9}$$

Here G is the elasticity modulus of the material and ε the deformation. Equation (8) is obtained from this by taking $\varepsilon = \text{const}$. The case where $\sigma = \text{const}$. corresponds to creep at constant stress. By substituting in (9) the expression for $n(U_1)$ from (7) we obtain, at $\sigma = \text{const}$.:

$$\frac{d\varepsilon}{dt} = \left(\frac{d\varepsilon}{dt}\right)_B + \left(\frac{d\varepsilon}{dt}\right)_j = \frac{\sigma}{G}\left[\frac{kT}{h} e^{-U/kT} + \frac{j \cdot 2 \times 10^{-2} q^{2/3}}{N_0 (U - \gamma\sigma)^{2/3}}\right]. \tag{10}$$

The first and second terms correspond to the ordinary creep rate, $(d\varepsilon/dt)_B$, and the increase in creep rate during irradiation, $(d\varepsilon/dt)_j$.

By substituting the values of the constants G, U_0 and γ it is possible to construct graphs of the dependence of $d\varepsilon/dt$ and relaxation time on temperature, stress and radiation intensity.

Figures 1 and 2 show some of these relationships. The values of the constants taken were $U_0 = 1$ ev and $\gamma = 10^{-21}$ cm^3.

Figure 2 shows the dependence of relaxation time, τ, on temperature, determined from equation (8) (at very low stresses) by the expression

$$\tau = \frac{N_0}{h} \frac{1}{(kT/h)e^{-U/kT} + j \cdot 2w^{-2} N_0^{-1} q^{2/3} U^{-2/3}}. \tag{11}$$

A similar expression is obtained for the relaxation time of a system in which an arbitrary kinetic process is proceeding (for example diffusion). Regions of strong and weak effects of radiation on the relaxation time of the system are seen in Fig. 2. The boundary between these regions is moved toward the high temperature region with increasing radiation intensity j.

Fig. 3 shows the dependence on temperature of the creep rate under irradiation at various stresses. The vertical axis represents the logarithm of the ratio of the creep rate, in sec^{-1}, to the elastic deformation. 1 is for $\sigma \to 0$, 2 for $\sigma = 2$ kg/mm² and 3 for $\sigma = 4$ kg/mm². 1′, 2′ and 3′ correspond to the same stresses but the radiation intensity is zero. It is seen that in the low temperature region where the creep rate is determined mainly by the radiation, the dependence of creep rate on stress is very slight. In the high temperature region where the rate of irradiation is small the ordinary exponential dependence is observed. The boundary between the regions moves toward the low temperature side with increasing stress. Qualitatively similar relationships are observed experimentally (see [2]).

The effect of irradiation on the spectrum of relaxation times. So far we have examined the effect of a radiation field on a material, the mechanical properties of which are portrayed by a simplified model—a single relaxation mechanism. In reality a satisfactory portrayal can be obtained only by the use of a rather wide, continuous set of relaxation mechanisms. It is easy to generalize the results obtained above to this case. A model consisting of an infinite number of Maxwell

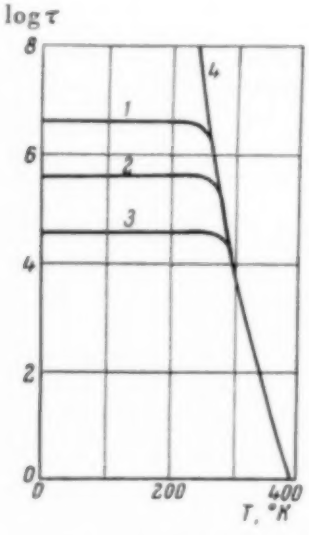

FIG. 2. Dependence of relaxation time on temperature at various radiation intensities. 1, 2, 3—intensities 5×10^5, 5×10^6 and 5×10^7 ergs. g^{-1} sec^{-1} respectively, 4—intensity zero.

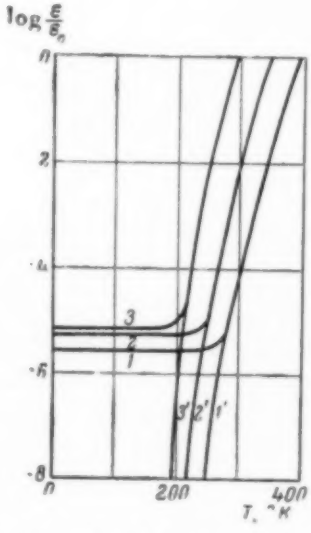

FIG. 3. Dependence of creep rate on temperature at a radiation intensity of 5×10^6 ergs. g^{-1} sec^{-1} and various stresses, σ.

elements in parallel, can be described, as is known [11], by a relaxation-time distribution function. Let us write this as $F(\nu)$, where $\nu = 1/\tau$. The case of the model with a single relaxation time, analysed above, corresponds to a distribution function of the form $F(\nu) = G_1\delta(\nu - \nu_1)$, where $\nu_1 = \nu_0 e^{-U_1/kt}$ and $\delta(\nu - \nu_1)$ is a delta function. The action of radiation leads to an increase in the relaxation frequency ν_1 by a quantity $\Delta(U) = \dot{j} \cdot 2 \times 10^{-2} \cdot N^{-1} q^{3/5} U^{-1/5}$. The distribution function of an irradiated material takes the form

$$F_j(\nu) = G_1\delta(\nu - \nu_1 - \Delta(U_1)) = F(\nu - \Delta(U_1))$$

It is obvious that for an arbitrary selection of relaxation mechanisms with a single activation energy U_1^* the distribution function takes the form

$$F_j(\nu) = F(\nu - \Delta(U_1)) \tag{12}$$

From the general equation describing the behaviour of a material with a selection of relaxation times

$$\sigma(t) = \int_0^\infty F(\nu)\, d\nu \int_{-\infty}^{t} \frac{d\varepsilon}{dt'}(t) e^{\nu(t'-t)}\, dt' \tag{13}$$

it is easy to obtain expressions for the various mechanical characteristics.

(a) For the kernel of the integrated Boltzman equation we obtain

$$\Phi(t-t') = \int_0^\infty d\nu F(\nu) e^{(t'-t)\nu}. \tag{14}$$

In the portrayal of an irradiated material $F(\nu)$ is substituted by $F_j(\nu) = F(\nu - \Delta)$. In as much as the given selection with a single activation energy Δ is independent of ν. Inserting the expression for $F_j(\nu)$ in the integral (14) and making the transformation $\nu - \Delta = \mu$ we obtain

$$\Phi_j(t-t') = \int_0^\infty d\nu F(\nu-\Delta)\, e^{(t'-t)\nu} = \int_0^\infty d\mu F(\mu) e^{(t'-t)(\mu+\Delta)} = e^{(t'-t)\Delta} \int_0^\infty d_\mu F(\mu) e^{(t'-t)\mu}.$$

Finally

$$\Phi_j(t-t') = e^{-(t'-t)\Delta}\, \Phi(t-t'). \tag{15}$$

(We have taken advantage of the fact that $F(\nu) = 0$ when $\nu < 0$)

(b) For the relaxation of stress at constant deformation we obtain similarly

$$\sigma_j(t) = e^{-t\Delta}\sigma(t). \tag{16}$$

(c) From the integrated Boltzman equation

$$\sigma(t) = \int_{-\infty}^{t} dt' \frac{d\varepsilon(t')}{dt'}\, \Phi(t-t'). \tag{16a}$$

* Selections of this type are suitable for the approximate analysis of experimental data [11].

When $\varepsilon(t') = \varepsilon_0 e^{i\omega t'}$ the following expression is obtained for the complex dynamic modulus of the material under ordinary conditions.

$$G(\omega) = i\omega \int_0^\infty dx \Phi(x) e^{-i\omega x} \tag{17}$$

and under radiation conditions

$$G_j(\omega) = i\omega \int_0^\infty dx \Phi_j(x) e^{-i\omega x} = i\omega \int_0^\infty dx e^{-x\Delta} \Phi(x) e^{-i\omega x}.$$

Or

$$G_j(\omega) = \frac{G(\omega - i\Delta)}{1 - i\dfrac{\Delta}{\omega}}. \tag{18}*$$

In the particular case of a single relaxation mechanism we have:

$$F(\nu) = G_1 \delta(\nu - \nu_1); \qquad G(\omega) = \frac{G_1}{1 - i\dfrac{\nu_1}{\omega}}; \qquad G_j(\omega) = \frac{G_1}{1 - i\dfrac{\nu_1 + \Delta}{\omega}}. \tag{18a}$$

Whence the tangent of the angle of mechanical loss

$$\tan\delta = \frac{\operatorname{Im} G(\omega)}{\operatorname{Re} G(\omega)} = \frac{\nu_1}{\omega}, \tag{18b}$$

and in the case of irradiation

$$(\tan\delta)_j = \frac{\nu_1 + \Delta}{\omega} = \tan\delta + \frac{\Delta}{\omega}. \tag{19}$$

Similar calculations can also be made for a model consisting of an infinite number of Kelvin elements in series.

From the equations obtained the following general conclusions can be drawn (for a material with a set of relaxation times having a single activation energy).

(1) The application of a radiation field alters the relaxation-time distribution function (displacing it in the direction of larger relaxation frequencies, ν).

Such a change in the distribution function cannot be brought about by simple heating up of the material (except in the case of a single relaxation mechanism) because on heating a material from a temperature T_1 to T_2 the distribution function is transformed according to the equation

$$F(\nu, T_2) = \frac{1}{z_{12}} F\left(\frac{\nu}{z_{12}}, T_1\right),$$

where

$$z_{12} = e^{\frac{U}{k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}. \tag{19a}$$

It can be shown also that the effect of irradiation on the glass temperature T_g (at the radiation intensities attainable) will be insignificantly small.

* Similar expressions are obtained also for the complex dielectric permeability of a material.

Other kinetic processes. Conclusions. The conception of the thermal activation of kinetic processes by irradiation can be applied also to the problem of the life of a material under load.

If, in conformity with Zhurkov and his collaborators (see [10]) degradation is regarded as a kinetic process then, as follows from equation (7), its rate will be increased by irradiation.

The life of a material under load in a radiation field will be expressed in this case as:

$$\tau_{degr}(\sigma) = \frac{B}{\frac{kT}{h} e^{-U/kT} + j \cdot 2 \times 10^{-2} N_0^{-1} q^{2/3} U^{-1/3}}, \tag{20}$$

where $U = U_0 - \gamma\sigma$ and $B \frac{h}{kt} e^{-(U_0 - \gamma\sigma)/kt}$ is the usual expression for the life at $j = 0$. Corresponding to the shortening of the life of the material there is a certain lowering of its breaking strength under extension at constant rate, during irradiation. This effect was observed in polymethyl-methacrylate (see [2]). Direct measurement of durability under radiation conditions would require methods enabling short life times to be measured because with large radiation intensities (tens of thousands of rads per sec) in many materials large irreversible changes of structure and mechanical properties build up after a few minutes, and these mask the reversible effects.

The above conceptions are applicable to other kinetic processes e.g. dielectric polarization, many chemical reactions, diffusion* etc.

It should be borne in mind, however, that we have assumed the applicability of Eyring's scheme for calculating the rates of kinetic processes in solid bodies. It is known that this is not strictly justified. Consequently the conclusions are doubly qualitative in character. The following, however, is without doubt. The radiation component of the rate of a kinetic process decreases with increasing activation energy of the process, but the intrinsic rate of the process (without irradiation) decreases considerably faster. Consequently the effect of acceleration of kinetic processes by irradiation becomes marked when the activation energies are high (or at low temperatures).

When metals are subjected to irradiation the number of atoms in the lattice possessing high energies (as a result of absorption of radiation) is some orders lower than in the case of dielectrics, because of the high electronic thermal conductivity of metals.

Irradiation can accelerate reactions involving free radicals produced by the radiation itself. It is known that some radicals produced by the irradiation of polymers at $T = 77°K$ are stable at that temperature (life-times calculated in months) (see [13] and [14]). Consequently on irradiation the concentration of free radicals will continue to increase for a long time in proportion to the ir-

* The change in diffusion constant in metals under irradiation was calculated in [12].

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radiation time. However at very high radiation intensities the life-time of the free radicals produced by the radiation can be reduced, at this temperature, to hours or minutes, which results in the establishment of a stationary concentration of radicals over a time period of this order. On increasing the radiation intensity further the concentration of free radicals increases very little. After cessation of irradiation the life-time of the radicals will increase to the normal value and their concentration will fall slowly or even remain practically constant. Obviously this can explain the phenomenon observed by Buben, Voyevodskii and collaborators [14]* of saturation of radical concentration in some substances on irradiation by a powerful electron beam, with no fall in concentration on cessation of irradiation.

The authors express deep gratitude to Iu. S. Lazurkin for constant discussions and valuable advice in this work.

CONCLUSIONS

(1) The acceleration of kinetic processes by irradiation is discussed in terms of the theory of absolute rate processes, taking into account the fact that materials under irradiation have an increased concentration of "hot" molecules.

(2) Expressions are derived describing the reversible changes in the mechanical relaxation properties of a material under irradiation.

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THE THERMAL DEGRADATION OF STEREOREGULAR POLYPROPYLENE*

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THE thermal degradation of stereoregular polypropylene has been studied in vacuo by means of an apparatus described previously [1], and also in air by the gravimetric method.

A whole series of volatile and involatile products are formed [2[in the degradation of polypropylene *in vacuo* at sufficiently high temperatures (Fig. 1). The diagram shows degradation rate curves obtained by measuring the total volatile decomposition products manometrically. Figure 2 shows integral curves of the degree of degradation as a function of time. These curves represent the true degradation kinetics only under conditions where the composition of the decomposition products changes only slightly with the degree of degradation. According to our measurements the energy of activation of the thermal degradation of stereoregular polypropylene *in vacuo* is 62,500 cal/mole. This is in good agreement with the figure of 61,000 cal/mole found by Madorsky [2] who studied the degradation of polypropylene *in vacuo*, using a tungsten spiral balance. This confirms the suitability of the manometric method for the study of the degradation of this polymer.

The presence of oxygen alters the degradation kinetics radically. As the curves of Fig. 3a show, on heating stereoregular polypropylene in air degradation begins at much lower temperatures than it does *in vacuo*. Already at 160° about half of the original polymer is decomposed in 5–6 hours whereas *in vacuo* at temperatures in the region of 380° about 30% of the polymer is decomposed.

It is interesting to note the existence of an induction period at 120° and below (Fig. 3a). The inflexion of the kinetic curves corresponds to a change in properties of the residual product. It changes from a colourless, viscous and gummy material to a deeply coloured solid. Figure 3b shows the dependence of the degree of degradation of polypropylene on film thickness, in air at 150°, over 4 hours. The characteristic picture of surface degradation of a polymer is seen. All these facts indicate that on heating polypropylene in air it is degraded oxid-

* Vysokomol. soedin. **2**: No. 1, 130–132, 1960.

atively. The induction period is more clearly defined at lower temperatures and this is connected with the accumulation of peroxides in the polymer, that act as secondary initiators of degradation.

We did not find any difference between the degradation of crystalline and amorphous polypropylene in air (the separation of the amorphous and crystalline polymers was effected by extraction with toluene at 20°C [3]). Neither could we find any significant effect on degradation, of the titanium compounds that are likely to be present in the commercial polymer, prepared by means of Ziegler catalysts. This series of experiments was carried out in the following way. A solution of $TiCl_4$ was heated gently, the hydrolysis product (a mixture of titanium oxide and hydroxide) was dried at 80° and then added to a solution of polypropylene (1—10%) in toluene, from which a film was poured.

In order to reduce the degradation of polypropylene in air an inhibitor of the antioxidant type should be used. For this purpose we incorporated certain

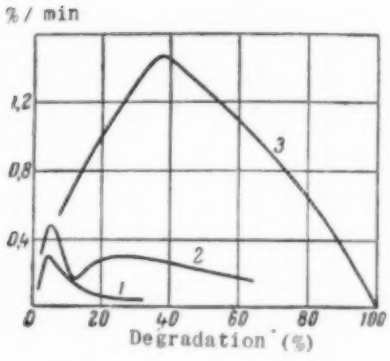

FIG. 1. Kinetic curves of the degradation of stereoregular polypropylene *in vacuo* (1) 380°, (2) 390°, (3) 425°C.

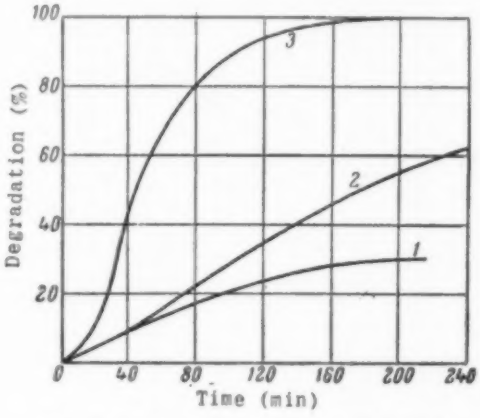

FIG. 2. Integral kinetic curves of degradation *in vacuo*. (1) 380°, (2) 390°, (3) 425°C.

compounds of this type in the polypropylene film. It was found that *p*-tert.-butylphenol, which is considered to be a powerful antioxidant, accelerates the oxidative degradation of polypropylene at 150°C. Evidently at high temperatures such substances react with oxygen and themselves form sources of radicals.

For the suppression of oxidative degradation antioxidants of low activity at room temperature should be incorporated in the polymer. Examples of such antioxidants are 2,2-di-(4-hydroxyphenyl) propane and di-(4-hydroxyphenyl) sulphide. The results of experiments with these are shown in Figure 4. The introduction of 1·5% of 2,2-di-(4-hydroxyphenyl) propane results in a sevenfold reduction in the degree of degradation in 4 hours at 150° (curve 5). Di-(4-hydroxy-

phenyl) sulphide has an even greater effect. As little as 0·1% of this antioxidant completely suppresses degradation of polypropylene for approximately two hours and 1% of di-(-hydroxyphenyl) sulphide completely inhibits oxidative degradation of the polymer for more than ten hours.

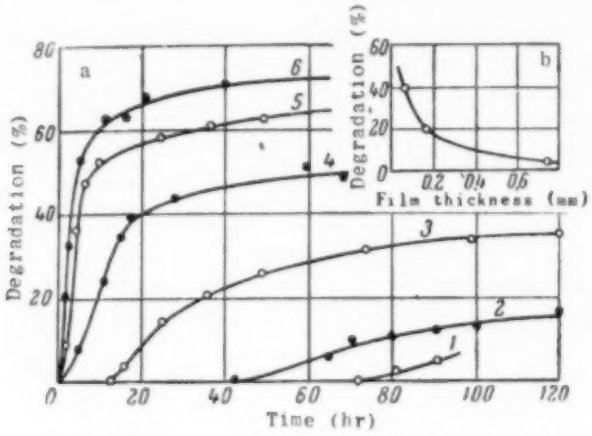

FIG. 3. Degradation of stereoregular polypropylene in air: (a) kinetic curves, of powders 0·5–1·0 mm. (1) 100°, (2) 110°, (3) 120°, (4) 140°, (5) 160°, (6) 180°C; (b) the dependence of degree of degradation on film thickness.

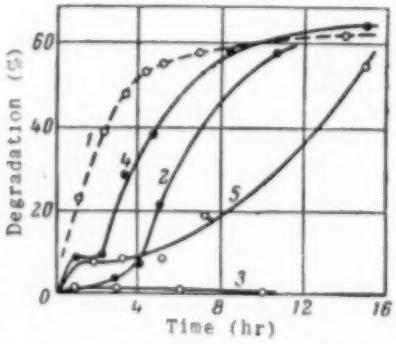

FIG. 4. The inhibition of oxidative degradation of stereoregular polypropylene at 150°: (1) pure polypropylene; (2) with 0·1% of di-(4-hydroxyphenyl) sulphide; (3) with 1·0% of di-(4-hydroxyphenyl) sulphide; (4) with 0·1% of 2,2-di-(4-hydroxyphenyl) propane; (5) with 1·5% of 2,2-di-(4-hydroxyphenyl) propane.

CONCLUSIONS

(1) Although polypropylene is fairly heat stable in vacuo, on heating this polymer in air vigorous oxidative degradation occurs.

(2) No difference is observed between amorphous and crystalline polypropylene with respect to degradation in the presence of oxygen.

(3) Titanium oxide residues, which are likely to be present in commercial samples of polypropylene produced with Ziegler catalysts, have no effect on the degradation of the polymer.

(4) Antioxidants of low activity at room temperature should be used as inhibitors of oxidative degradation of polymers. In particular, di-(4-hydroxyphenyl) sulphide strongly inhibits the oxidative degradation of polypropylene.

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POLYMERIZATION ON A POTASSIUM–CARBON BLACK CATALYST*

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THERE is a large amount of information in the literature on polymerization on alkali metals. In work reported in the literature polymerization has been brought about by the use of the free metals in the form of thin coatings or suspensions in inert solvents, and also in solution in liquid ammonia.

In catalytic polymerization the degree of dispersion of the catalyst is of great importance. The limiting degree of dispersion is attained in solution. However liquid ammonia, a typical solvent for alkali metals, is not inert and can take part in the polymerization reactions.

In our work, in order to obtain highly dispersed, heterogeneous catalysts, suitable for polymerizations in inert solvents, products from the interaction of potassium with carbon black were used.

The products of the interaction of alkali metals with carbon (in the form of graphite, carbon black or activated carbon) are compounds of variable composition in which the graphite lattice is preserved but with a somewhat greater separation of the planes and with alkali metal atoms distributed in layers between the layers of carbon atoms [1,2]. The use of these compounds as polymerization initiators has been studied little. (Recently a paper was published on their use in the polymerization of ethylene [3]).

Products from the interaction of potassium with carbon black, in which the ratio of potassium to carbon black was varied from 1:6 to 1:10 were studied as polymerization catalysts. The catalysts were prepared in the apparatus shown in Fig. 1. The sealed ampoule 3, containing a weighed quantity of potassium, was placed inside ampoule 2; the calculated quantity of carbon black and the magnetic stirrer 6 were placed in ampoule 1 which is fitted with a side tube with a thin, glass partition 4, and connected to a vacuum pump through the outlet 5. The two ampoules were sealed and the potassium was then distilled *in vacuo* into ampoule 1. After this ampoule 2 was sealed off at the constriction 7 and ampoule 1 was sealed off from the vacuum pump at 8.

Ampoule 1, containing potassium and carbon black in a chosen ratio, was held at 250° in a thermostat for 5 hr. Complete homogenization of the mixture was achieved under these conditions and the catalyst was ready for use.

Polymerization was carried out in the apparatus shown in Fig. 2. Ampoule 1 containing the catalyst was sealed on to the vacuum system, though separated

* Vysokomol. soedin. **2**: No. 1, 162–165, 1960.

from it by the thin glass partition 3 which could be broken at the desired moment by the magnetic breaker 2. The solvent was placed in ampoule 4 and the monomer in ampoule 5. The two ampoules were sealed and the monomer and solvent were thoroughly degassed by repeated freezing under high vacuum. Tap 6 was then closed, the thin glass partition 3 was broken and the solvent was distilled into the ampoule containing the catalyst. This ampoule was brought to the required temperature by immersing it in a bath of propyl alcohol 7, cooled externally by liquid nitrogen. Tap 6 was then opened and the monomer was distilled into the catalyst ampoule. The polymerization was run for 2 hr with continuous stirring.

At the end of this period the cooled ampoule 1 containing the reaction mixture was opened and the catalyst was decomposed by the addition of methanol. By this means it was possible to avoid the formation of polymer at temperatures above that of the experiment. The polymer isolated from the reaction mixture was thoroughly freed from catalyst and dried.

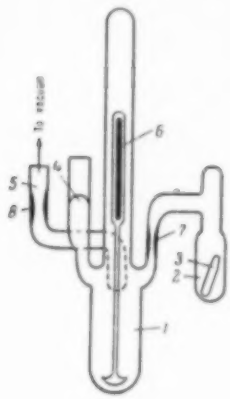


Fig. 1.

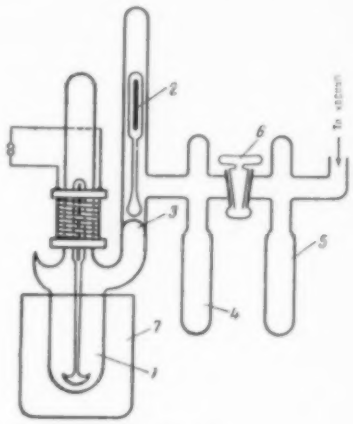


Fig. 2.

In all the experiments the molar ratio of monomer to potassium was 10:1 and the volume of solvent used was equal to that of the monomer.

Experiments were carried out on the polymerization of a number of monomers in toluene at various temperatures. The experimental results are given in Table 1.

As Table 1 shows, the reaction product of potassium and carbon black is capable of initiating the polymerization of monomers containing strongly electronegative groups (methyl methacrylate, methyl acrylate, acrylonitrile) at temperatures down to −85°. Styrene and α-methylstyrene did not polymerize under these conditions at low temperatures. However at 20° styrene polymerizes instantaneously and practically completely. In the presence of 0·04 per cent of hydroquinone, calculated on the monomer, the yield of polymethylmethacrylate

TABLE 1. POLYMERIZATION OF MONOMERS IN TOLUENE AT VARIOUS TEMPERATURES

Monomer	Molar ratio of potassium: carbon black	Temperature (°C)	Yield of solid polymer (%)	$[\eta]$ at 20°C
				(acetone)
Methyl methacrylate	1:9	−20 — −22	87	0·62
	1:6	−42 — −44	40	0·64
	1:8	−60	36·5	0·66
	1:9	−85	36	0·68
				(dimethyl-formamide)
Acrylonitrile	1:7	0 — — 5	22	0·12
	1:9	−60	3·5	0·23
	1:8	−85	1	0·32
				(acetone)
Methylacrylate	1:8	−85	17·4	0·13
Vinylacetate	1:8	−60	Trace	—
Methylstyrene	1:6	−60	None	—
Styrene	1:7	+20	100	
	1:6	−60	None	—
Methylmethacrylate + 0·04% hydroquinone	1:9	−85	9	—
The same + 0·55% hydroquinone	1:9	−85	9	—
Styrene + 0·85% hydroquinone	1:10	+20	100	—

$$\xleftarrow{\text{anionic chain growth}} \overset{+}{\text{Me}}\text{CH}_2-\underset{\displaystyle \text{R}}{\overset{\displaystyle \cdot}{\text{C}}}\text{H} \xrightarrow{\text{radical chain growth}}$$

falls by a factor of approximately 4. A 14-fold increase in the quantity of hydroquinone caused no further lowering of the yield. At 20° styrene polymerizes practically completely even in the presence of 0·85 per cent of hydroquinone.

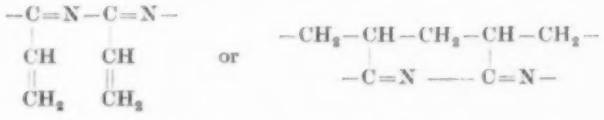
There are evidently different mechanisms of polymerization for different types of monomer in the presence of the potassium–carbon black catalyst. We assume that in our system the polymerization of monomers with strongly electronegative groups is brought about by radical-ions of the type $\text{R-}\dot{\text{C}}\text{H-}\bar{\text{C}}\text{H}_2$ formed by transfer of an electron from the conductivity zone of the catalyst to a monomer molecule adsorbed on its surface. The suggestion of the formation of radical-ions in the polymerization of butadiene, styrene and isoprene in the presence of a sodium-naphthalene complex was first put forward in [4]. Subsequently a number of authors have made use of this idea to explain the experimental results of polymerization and copolymerization in the presence of alkali metals and their solutions in liquid ammonia [5, 6]. In this connexion it was shown that

in the copolymerization of styrene and methyl methacrylate by lithium in media of low dielectric constant, chain growth can take place by ionic and radical mechanisms simultaneously [6].

This dual type of polymerization evidently occurs in our systems also, in the case of polymerization of monomers with strongly electronegative substituents. In this case the radical-ions formed can become adsorbed on to the surface of the carbon black and this hinders their recombination. The addition of hydroquinone in sufficient quantity inhibits radical polymerization but anionic chain growth proceeds even in the presence of hydroquinone. The addition of a radical inhibitor has no effect on the anionic process. In this case the formation of the potassium salt of hydroquinone evidently does not poison the catalyst because new potassium atoms readily diffuse from the depth of the carbon black particles in place of those reacted. At the same time the hydroquinone salt molecules appear to be capable of terminating the radical chains.

In the case of polymerization of styrene at low temperatures it is evident that there is practically no radical-ion formation in this system. On the other hand this process becomes sufficiently effective at 20°, resulting in the rapid, anionic polymerization of the styrene, which is not inhibited by hydroquinone. More exact conclusions about the mechanism of polymerization in the presence of potassium–carbon black will be obtained from a study of the copolymerization of various monomers.

An X-ray diffraction examination of samples of polyacrylonitrile obtained under these conditions has shown that its structure is less ordered than that of ordinary polyacrylonitrile obtained by bulk polymerization with benzoyl peroxide at 80°C. A possible source of irregularity in the case of the potassium–carbon black catalyst is the possibility that in addition to polymerization through the C=C bonds polymerization can also take place through the nitrile bonds with the formation of groups of the composition:



This is supported by the yellow colour of the polymer [7].

CONCLUSIONS

The polymerization of a number of monomers in toluene in the presence of potassium–carbon black as catalyst has been studied.

This catalyst brings about polymerization at low temperatures of vinyl monomers containing strongly electronegative groups (methyl methacrylate, methyl acrylate, acrylonitrile).

It is suggested that polymerization of these monomers proceeds by a radical-ion mechanism.

In the presence of this catalyst rapid polymerizaton of styrene occurs at 20°C. An anionic mechanism is proposed for this process.

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THE STABILIZATION OF POLYVINYLCHLORIDE BY AUTOCONDENSATION PRODUCTS OF CYCLOHEXANONE*

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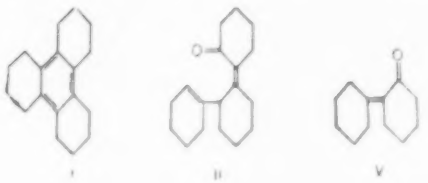
THE action of heat or light on polyvinylchloride during processing, or on articles made from polyvinylchloride during use, causes degradation of the polymer. Since both dehydrochlorination and oxidation occur during degradation, for the stabilization of polyvinylchloride, it is necessary to add antioxidants in addition to substances that suppress dehydrochlorination. Organic compounds containing nitrogen [1, 2] have been widely used as antioxidants for the stabilization of high-molecular compounds. Some of these are used also for stabilization of polyvinylchloride [3]. It is known, however, that organic compounds containing nitrogen accelerate the thermal decomposition of halogen-containing polymers [4].

Recently an increasing amount of information is appearing in the literature on the use, as stabilizers for polyvinylchloride, of organic compounds, not containing nitrogen, that absorb in the UV region of the spectrum [5, 6]. Among such compounds is 2-cyclohexylidenecyclohexanone, an autocondensation product of cyclohexanone, that has not, however, found practical application because of its volatility and poor compatibility with polymers.

In this work the stabilizing action has been investigated of the following autocondensation products of cyclohexanone, that are involatile and of good compatibility with polyvinylchloride: 1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotriphenylene (I), 2-2-(*Δ*′-cyclohexanyl)-cyclohexylidene-cyclohexanone (II) and the product of condensation of six molecules of cyclohexanone, with a molecular weight of 500–550 (III), the structure of which has not been fully established [7].



For a comparative evaluation of the stabilizing activity of products I, II and III the stabilizing action of 2-cyclohexylidenecyclohexanone (IV), 2,4-dihydroxybenzophenone (V), 2,4,6-trihydroxybenzophenone (VI), 2,4-dihydroxyacetophenone (VII) and resorcinyl dibenzoate (VIII) was also examined.

* Vysokomol. soedin. **2**: No. 2, 210–215, 1960.

EXPERIMENTAL

The stabilizing action of the antioxidants was determined in "PF-special" grade of polyvinylchloride (PVC) in powder form and plasticized with plasticizer ED-242.

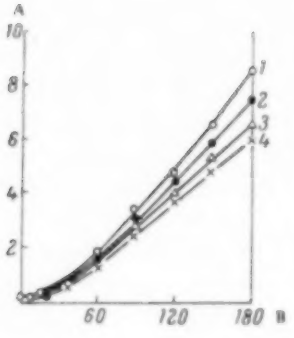


Fig. 1. Rate of dehydrochlorination of PVC at 175° in a current of air in the presence of cyclohexanone autocondensation products (I, II and III): (A) quantity of HCl in mg per 1 g PVC; (B) time of heating in minutes; (1) PVC without antioxidant; (2) with antioxidant I; (3) with antioxidant II; (4) with antioxidant III (0·00025 moles antioxidant per 10 g PVC)

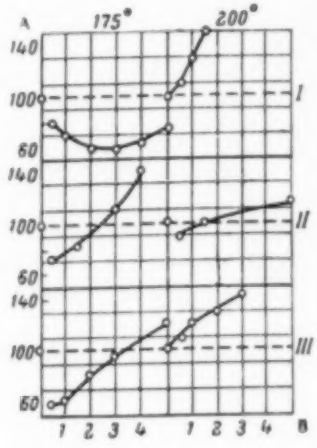


Fig. 2. Rate of decomposition of PVC at 175 and 200° in a current of air in the presence of different amounts of antioxidants I, II and III: (A) rate of decomposition of PVC, in % relative to the rate of decomposition of unstabilized PVC; (B) concentration of antioxidant in parts by weight per 100 parts by weight of PVC.

The PVC was decomposed at 175° in a current of air and the heat stability was determined, i.e. the length of the induction period before commencement of evolution of hydrogen chloride (qualitatively, by Congo), and the rate of evolution of free hydrogen chloride—V.

V was found from the mean integrated ordinate from a plot of A—the quantity of HCl evolved in mg from 1 g of PVC, against B—the time of heating in minutes.

In all cases the sample was held at 175° for 180 minutes. The ratio $V/V_0 \times 100\%$ (where V_0 is the rate of evolution of HCl from unstabilized PVC) characterizes the reduction in rate of evolution of HCl as a result of addition of the stabilizer. The quantity of HCl was determined as chloride ions by titration against 0·001 N silver nitrate solution, with a mercury-silver electrode.

The decomposition temperature of the samples was determined by heating the polymer up to commencement of decomposition (as shown by the appearance of turbidity in a silver nitrate solution).

TABLE 1. STABILIZING ACTION OF ANTIOXIDANTS

Antioxidant	Quantity per 10g of PVC (g)	Decomposition temperature of PVC (°C)	Time of UV-irradiation of PVC (hr)	Heat stability at 175°C	$V\left(\frac{\text{mg HCL}}{\text{1 g PVC}}\right)$	$\frac{V}{V_0}\cdot 100$ (%)
PVC without antioxidant	—	168	—	7·0	5·2	100
			4	1·5	8·6	100
			—	7·0	4·2	81
I	0·0600	171	4	1·5	6·7	78
			—	5	3·4	65
II	0·0645	155	4	1	5·8	67
			—	7	3·2	62
III	0·1290	168	4	2	6·4	74
			—	6	3·9	75
IV	0·0445	167	4	1·5	8·0	93
			—	8	4·6	88
V	0·0543	162	4	2	8·4	98
			—	7	3·0	58
VI	0·0560	170	4	1·5	6·0	70
			—	7	4·1	79
VII	0·0380	163	4	1·5	7·4	86
			—	7	5·0	96
VIII	0·0795	170	4	1·5	8·5	99

TABLE 2. ACTIVITY OF PRODUCTS I, II AND III AFTER TREATMENT WITH HCl AND UV-RADIATION

Antioxidant	Decomposition temperature of PVC (°C)	Time of UV-irradiation of PVC (hr)	Heat stability at 175° (min)	$V\left(\frac{\text{mg HCL}}{\text{1 g PVC}}\right)$	$\frac{V}{V_0}\cdot 100$ (%)
After treatment	170	—	9	3·5	73
		4	2	6·1	71
II The same	157	—	6	3·5	73
		4	2	6·1	71
III The same	170	—	7	3·2	67
		4	2	6·2	73
After UV-irradiation	170	—	6	4·1	86
		4	1·5	7·2	84
II The same	158	—	7·5	3·6	75
		4	2·0	6·9	80
III The same	169	—	6	3·1	65
		4	2	7·0	75

The light-stabilizing action was determined by the reduction in heat-stability and the increase in rate of evolution of hydrogen chloride from the PVC after irradiation of the stabilized and unstabilized polymer under a PRK-2 lamp.

TABLE 3. SYNERGISTIC ACTION OF ANTIOXIDANTS IN ADMIXTURE WITH LEAD SILICATE.
(CONCENTRATION OF STABILIZERS, 0·000125 MOLES PER 10 G PVC)

Stabilizers	Quantity in 10 g of PVC (g)	Temperature decomposition of PVC (°C)	Time of UV-irradiation of PVC (hr)	Heat stability at 175° (min)	$\frac{V}{\left(\frac{\text{mg HCl}}{1\text{ g PVC}}\right)}$	$\frac{V}{V_0}\cdot 100$ (%)	Synergistic action*		
							Decomposition temperature (°C)	Heat stability	$\frac{V}{V_0}\cdot 100$ (%)
Lead silicate	0·0354	189	—	15	3·4	66	182 / +7	15 / —	70 / +4
I	0·030		4	2·5	8·1	94		2·5 / —	83 / −11
Lead silicate	0·0354	191	—	15	3·0	58	174 / +17	14 / +1	62 / +4
II	0·0322		4	2	7·2	84		2 / —	78 / −6
Lead silicate	0·0354	188	—	16	2·7	52	180 / +8	15 / +1	60 / +8
III	0·0645		4	3	5·7	66		3 / —	81 / +15
Lead silicate	0·0354	185	—	17	3·0	58	180 / +5	15 / +2	66 / +8
IV	0·0222		4	4	7·3	85		2 / +2	90 / +5
Lead silicate	0·0354	193	—	18	3·6	69	177 / +16	16 / +2	78 / +4
V	0·0267		4	1·5	8·0	93		2·5 / −1	93 / —

* Numerator – values calculated on the assumption of the additivity of action of the stabilizers in the mixture. Denominator-Variation from additive values.

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TABLE 4. STABILIZING ACTION OF ANTIOXIDANTS I, II, III, IV AND V IN ADMIXTURE WITH LEAD SILICATE AND CALCIUM STEARATE

Stabilizer	Quantity per 100 g of PVC (g)	Decomposition temperature of plasticized polymer (°C)	Time of UV-irradiation of plasticized polymer (hr)	Heat stability of plasticized polymer at 275° (min)	$\frac{V}{\text{mg HCL}}{\text{1 g specimen}}$	$\frac{V}{V_0} \cdot 100$ (%)
Lead silicate	3	205	–	35–40	1·47	100
Calcium stearate	1		20	20–25	1·33	100
Lead silicate	3	205	–	70–80	0·40	30
Calcium stearate	1					
I	1		20	22–26	0·90	60
Lead silicate	3	208	–	100	0	0
Calcium stearate	1					
II	1		20	30–35	0·3	20
Lead silicate	3	206	–	130–140	0·11	10
Calcium stearate	1					
III	1		20	25–30	0·94	60
Lead silicate	3	205	–	70–80	0·77	50
Calcium stearate	1					
IV	1		20	20–25	1·28	80
Lead silicate	3	204	–	90–100	0·30	20
Calcium stearate	1					
V	1		20	20–25	0·26	20

The ability of the antioxidants to inhibit the decomposition of PVC was measured by the ratio of the rates of dehydrochlorination on heating the stabilized and unstabilized polymer. The rate of dehydrochlorination was determined from the total quantity of hydrogen chloride, liberated in the free state and remaining in the polymer. The chloride ion content in the polymer was determined by titration of a 1% solution of the PVC in a mixture of dioxan and cyclohexanone (1·0:0·6). An equal volume of doubly-distilled water was added to the polymer solution before titration.

Table 1 shows the stabilizing action of the antioxidants when added individually to the polymer powder in the proportion of 0.00025 moles in 10 g of PVC.

The inhibiting action of products I, II and III on the thermal decomposition of PVC is shown in Figure 1.

The dependence of the activity of these products on concentration and on the temperature at which decomposition of the PVC was carried out, is shown in Fig. 2.

The activity of products I, II and III was tested after treating them with hydrogen chloride at 175° for 10 hours, and also after irradiating them under a PRK-2 lamp for 10 hours, at a concentration of 0·1 g in 10 g of PVC (Table 2).

The activity of products I, II, III and IV in admixture with lead silicate and calcium stearate was determined (Tables 3 and 4) in tests with the powder (Table 3) and the plasticised material (Table 4).

DISCUSSION

The antioxidants tested decreased the rate of decomposition of polyvinylchloride by heat and light without affecting the temperature at which decomposition commences or the length of the induction period (Table 1). The stabilizing action of the antioxidants is not connected with the acceptance of hydrogen chloride, as is shown by their inertness toward HCl under conditions similar to those of the decomposition of polyvinylchloride. After treatment with hydrogen chloride at 175° for 10 hours the cyclohexanone autocondensation products I, II and III do not contain chlorine and they maintain their initial stabilizing activity (Table 2).

The activity of the cyclohexanone autocondensation products, like the other antioxidants tested, depends on their concentration and on temperature.

An increase in concentration above the optimal value for each of these antioxidants can give rise to an increased rate of decomposition of polyvinylchloride. The activity of the antioxidants falls with increasing temperature (see Fig. 2).

The combined use of the antioxidants with such stabilizers, widely used in industry, as lead silicate and calcium stearate, shows a synergistic action (Table 3). The addition of the cyclohexanone autocondensation products to the plasticized polymer substantially increases its stability to heat and light without affecting its physicomechanical constants. The stabilizing action of the cyclohexanone

autocondensation products is so marked that it is not masked even by large quantities of a powerful stabilizer such as lead silicate. For example, the addition of 0·5 parts by weight of antioxidant to the plasticized polymer (containing 12 parts by weight of lead silicate and 3 parts by weight of calcium stearate to 100 parts by weight of PVC) brings about an increase in heat stability at 175° from 190 to 220 minutes for product I, 250 minutes for product II and 290 minutes for product III.

CONCLUSIONS

(1) The cyclohexanone autocondensation products 1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotriphenylene, 2-2-(*Δ'*-cyclohexenyl)-cycohexylidene-cyclohexanone and the condensation product of six molecules of cyclohexanone, of molecular weight 500–550, have been examined as antioxidant-stabilizers of polyvinylchloride.

The above products are inhibitors of the light and thermal decomposition of polyvinylchloride. They decrease the rate of decomposition of the polymer without affecting the temperature at which degradation commences, or the length of the induction period.

(2) The stabilizing action of the cyclohexanone autocondensation products is not connected with the acceptance of hydrogen chloride. While being effective inhibitors at optimal concentrations and temperatures these antioxidants can give rise to an increased rate of decomposition if used in concentrations considerably above the optimal, and also at 190–200°C.

(3) When the cyclohexanone autocondensation products are used in admixture with such widely used stabilizers as lead silicate and calcium stearate a synergistic action is observed.

(4) The addition of the cyclohexanone autocondensation products to plasticized polyvinylchloride brings about a considerable improvement in its light and heat stability.

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REACTIONS OF CARBOXYLATED BUTADIENE-STYRENE RUBBERS UNDER THE ACTION OF γ-RADIATION*

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CARBOXYLATED butadiene-styrene rubbers (KBSK) possess a whole series of specific properties in comparison with ordinary butadiene-styrene rubbers (BSK). Above all the possibility of crosslinking KBSK by oxides and metal salts, including those of monovalent metals [1], diamines and other bifunctional reagents, should be noted. The presence of carboxyl groups in the polymer chain enables a whole series of reactions to be carried out with KBSK, including radiochemical reactions. It is known [2] that under the action of ionizing radiation compounds containing carboxyl groups undergo two types of reaction. Firstly the molecule undergoes decarboxylation with subsequent formation of a hydrocarbon according to the scheme:

$$RCH_2COOH \longrightarrow RCH_3 + CO_2$$

Secondly dehydrogenation with formation of unsaturated acids is possible:

$$R(CH_2)_nCH_2CH_2(CH_2)_mCOOH \longrightarrow R(CH_2)_n-CH=CH-(CH_2)_m-COOH + H_2$$

The relationship between the two types of reaction depends on the structure of the original compound.

In the present work the radiochemical reactions of KBSK of various types under γ-radiation were studied. Irradiation was carried out with a ^{60}Co source of K-20 type, of output 2×10^4 c. The ferrous sulphate dosimetric reaction ($G = 15{\cdot}5 \pm 0{\cdot}3$ ions per 100 ev) was used for measurement of dosage. Samples of KBSK of different methacrylic acid content were cold-pressed to produce films of 0·5 mm thickness. The films were subjected to irradiation in dosages from 0·1 to 50 megaroentgens, in sealed ampoules in an atmosphere of argon containing 0·05 per cent oxygen. We determined the carboxyl group content of the irradiated samples by titrating with a solution of KOH in benzyl alcohol [3], the maximal swelling in benzene or methyl ethyl ketone, the gel content and the intrinsic viscosity of the sol fraction.

In this work rubbers containing 30% styrene and, by analysis, 1·30 and 1·60% methacrylic acid, and 50% styrene with 2·88 and 5·34% methacrylic

* Vysokomol. soedin. **2**: No. 2, 259–264, 1960.

acid were used. The rubbers were first purified by extraction with a binary mixture of toluene and ethyl alcohol (32:68) in an atmosphere of nitrogen for 40 hours.

Table 1 and Fig. 1 show the variation in carboxyl-group content during irradiation.

Table 2 and Fig. 2 show the variation in gel content during irradiation.

As is seen from Fig. 1 and Table 1 the effectiveness of decarboxylation is high at low dosages and gradually decreases with increasing dosage. The fact that the relationship between the rates of disappearance of carboxyl group and formation of gel is not linear indicates the complexity of the crosslinking mechanism and the occurrence of degradation processes. Degradation is marked

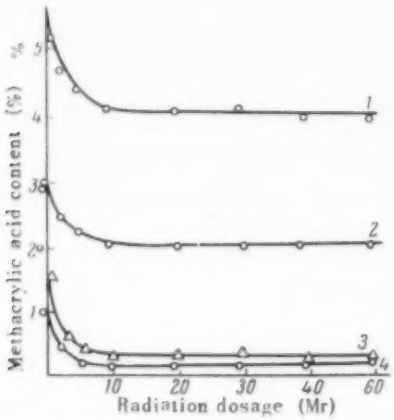

FIG. 1. Variation in carboxyl-group content with radiation dosage. Methacrylic acid content in original rubbers (1) 5·34%; (2) 2·88%; (3) 1·60%; (4) 1·30%.

at low radiation dosages, as the sharp fall in intrinsic viscosity of the sol fraction at low dosages indicates.

Figure 4 shows the variation in maximal swelling of the rubbers in methyl ethyl ketone or benzene with dosage. The curves of the dependence of maximal swelling in benzene, on dosage, have the same shape as those for the irradiation of SKS-30 rubber [4]. It is seen from these graphs and from Table 2 that crosslinking with the formation of insoluble gel occurs at dosages above 2·5 Mr. Increase in the quantity of methacrylic acid in the polymer leads to more intensive crosslinking (curves 1 and 2; 4 and 5; 7 and 8). At low dosages the difference between the density of crosslinking of BSK and KBSK is greater (curves 3, 4 and 5) and at dosages above 30 Mr there is practically no difference. The relative decrease in the proportion of crosslinking at the carboxyl groups in the later stages of network formation is obviously explained by steric hindrance resulting

from the decreased mobility of the chains after full gel formation. The rubbers swell to a considerably smaller extent in the polar solvent methyl ethyl ketone than in benzene, however the order of distribution of the curves corresponding to the different methacrylic-acid contents is preserved.

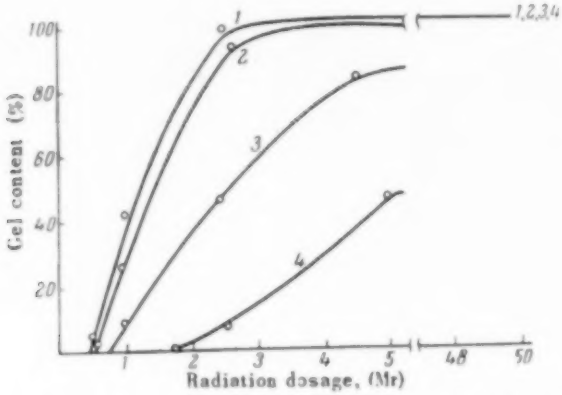

FIG. 2. Variation in gel content with radiation dosage: (1) KBSK with 50% styrene and 5·34% methacrylic acid; (2) KBSK with 50% styrene and 2·88% methacrylic acid; (3) SKS-50; (4) KBSK with 30% styrene and 1·60% methacrylic acid.

TABLE 1. VARIATION IN CARBOXYL GROUP CONTENT WITH RADIATION DOSAGE*

Irradiated Rubber	Dosage (Mr)									
	0·1	0·5	1	2·5	5	10	20	30	40	50
KBSK with 30% styrene and 1·30% methacrylic acid	0·97	0·50	0·37	0·29	0·22	0·17	0·15	0·15	0·14	0·13
KBSK with 30% styrene and 1·6% methacrylic acid	—	0·84	0·63	0·56	0·42	0·29	0·22	0·20	0·18	0·18
KBSK with 50% styrene and 2·88% methacrylic acid				2·56	2·40	2·32	2·22	2·20	2·15	2·09
KBSK with 50% styrene and 5·34% methacrylic acid				4·54	4·36	4·26	4·14	4·02	3·96	3·93

*The quantity of carboxyl groups is calculated as the methacrylic-acid content of the polymer (wt. %).

TABLE 2. VARIATION IN GEL CONTENT WITH RADIATION DOSAGE

Irradiated rubber	Dosage (Mr)									
	0·1	0·5	1	2·5	5	10	20	30	40	50
BSK with 50% styrene	—	—	7·0	47·0	82·0	98·0	100	100	100	100
KBSK with 30% styrene and 1·30% methacrylic acid			0·5	9·0	32·0	86·0	98·2	100	100	100
KBSK with 30% styrene and 1·6% methacrylic acid			0·2	6·0	46·0	88·0	99·4	100	100	100
KBSK with 50% styrene and 2·88% methacrylic acid		0·8	29·0	93·0	98·8	100	100	100	100	100
KBSK with 50% styrene and 5·34% methacrylic acid		2	42·0	97·0	99·5	100	100	100	100	100

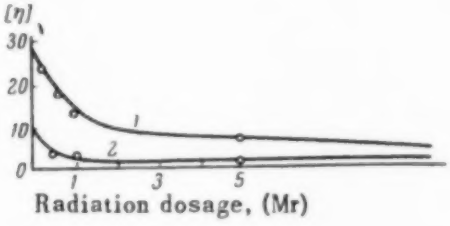

FIG. 3. Variation with radiation dosage of the intrinsic viscosity, in benzene solution, of the sol fractions of KBSK. (1) 1·30% methacrylic acid; (2) 1·60% methacrylic acid.

The results obtained indicate that the carboxyl groups take part in crosslinking. The G-value for the number of crosslinks at low dosages increases linearly with the carboxyl-group content of the original polymer (Table 3, Fig. 5). The slope of the lines decreases with increasing dosage, and this is evidently connected with a decrease in crosslinking through the carboxyl groups because of the decrease in the probability factor after formation of a three-dimensional network.

As is seen from Table 3 the number of crosslinks formed at low radiation dosages (up to 20 Mr) at the expense of carboxyl groups, as calculated from the maximum swelling, is in satisfactory agreement with the number calculated

from the loss of carboxyl groups. The number of crosslinks formed via the carboxyl groups in no case exceeds 30 per cent of the total number of crosslinks.

We suggest that crosslinking involving the carboxyl groups takes place in the following way.

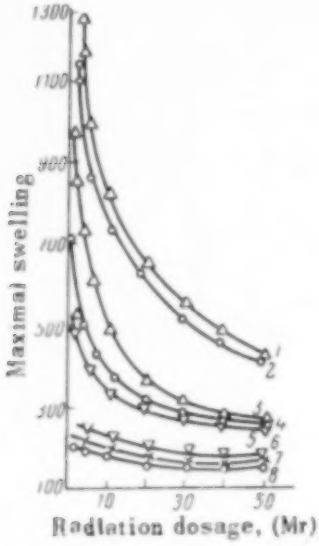

FIG. 4. Variation in maximal swelling of the rubbers, with radiation dosage. (1) KBSK with 30% styrene and 1·30% methacrylic acid, (2) KBSK with 30% styrene and 1·60% methacrylic acid, (3) and (6) SKS-50; (4) and (7) KBGK with 50% styrene and 2·88% methacrylic acid; (5) and (8) KBSK with 50% styrene and 5·34% methacrylic acid: (1)–(5) in benzene, (6)–(8) in methyl ethyl ketone.

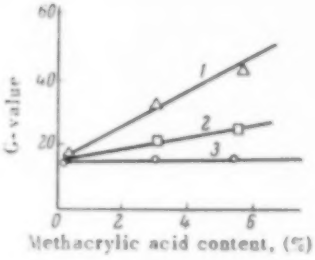

FIG. 5. Relationship between G-value and carboxyl-group content of original polymer. Radiation dosage: *1*—1·2–2·5, *2*—3–5, *3*—4–10 Mr.

A polymeric radical and a hydrogen atom are formed as the result of an act of decarboxylation:

$$RCOOH \xrightarrow{h\nu} R^{\cdot} + CO_2 + H^{\cdot}.$$

The polymeric radical formed interacts with a double bond of a rubber molecule or with a similar radical, and crosslinking results:

$$R^{\cdot} + CH_2-CH=CH-CH_2- \longrightarrow -CH_2-\underset{\displaystyle R}{\dot{C}H}-\dot{C}H-CH_2-R^{\cdot} + R_1^{\cdot} \longrightarrow RR_1$$

The hydrogen atoms combine, with liberation of gaseous hydrogen, and also take part in other reactions, for example the abstraction of an H atom from a polymer molecule with formation of H_2 [5].

In the above scheme those reactions that take place in the crosslinking of butadiene-styrene polymers that are free from carboxyl groups, are not considered.

TABLE 3. G-VALUE FOR THE NUMBER OF CROSS-LINKS FORMED ON IRRADIATION

Radiation dosage, (Mr)	Number of crosslinks	Original rubber		
		per 100 ev	in 1 molecule calculated from the swelling maximum	calculated from the loss of carboxyl groups
SKS-50, mol. wt. 192,000*	2·5	16·0	14	—
	5	17·1	26	—
	10	15·5	36	—
	20	16·0	100	—
	30	14·0	120	—
	40	11·0	136	—
	50	9·5	147	—
KBSK with 50% styrene and 2·88% methacrylic acid, mol. wt. 120,000	2·5	30·0	16	4·8
	5	32·0	37	7·7
	10	22·0	50	8·7
	20	16·5	66	10·2
	30	13·2	85	10·6
	40	13·2	85	12·3
	50	8·5	91	13·2
KBSK with 50% styrene and 5·34% methacrylic acid mol. wt. 110,000	2·5	47·0	24	13·5
	5	44·0	45	16·4
	10	25·0	61	17·1
	20	17·7	62	20·1
	30	14·4	80	22·1
	40	12·2	84	23·0
	50	12·2	84	23·6

* The mol. wt. was determined viscometrically according to the equation $[\eta] + [\mu] = 5.26 \times 10^{-4} M^{0.67}$.

CONCLUSIONS

(1) On irradiation of butadiene-styrene rubbers containing carboxyl groups (KBSK) to the extent of 1·30 and 1·60% of methacrylic acid in the 30% styrene polymer, and 2·88 and 5·34% in the 50% styrene polymer, with a ^{60}Co source at dosages up to 50 Mr a reduction in carboxyl-group content occurs and this is particularly marked at low dosages.

(2) The observed relationship between the quantity of gel formed and the loss of carboxyl groups indicates that the mechanism of crosslinking is complex and that degradation occurs. The latter is indicated by a fall in viscosity of the sol fraction, which is very marked at low dosages.

(3) An increase in the amount of methacrylic acid in the polymer leads to an increase in the degree of crosslinking. There is a linear relationship between the carboxyl group content of the rubber and the G-value with respect to crosslinks.

(4) On irradiation at dosages up to 20 Mr the number of crosslinks formed at the expense of carboxyl groups, calculated from the maximal swelling, is in satisfactory agreement with the number calculated from the loss of carboxyl groups.

Translated by E. O. PHILLIPS

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THE LIGHT SCATTERING AND VISCOSITY OF SOLUTIONS OF POLY-β-VINYLNAPHTHALENE IN AN IDEAL SOLVENT*

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INTRODUCTION

IT is known that an assessment of the flexibility of polymer chains can be made by determination of the dimensions of the polymeric molecules. For this purpose, in order to prevent the distorting effect of interaction with the solvent (various degrees of swelling) it is desirable to determine the dimensions in an ideal solvent.

The results of an investigation of the light scattering and viscosity of poly-*β*-vinylnaphthalene (PVN) in a good solvent, benzene, have been reported [3]. The dimensions of the PVN molecules in benzene, found by this means, were considerably greater than the normal dimensions of polyvinyl chains in solution. It was concluded on the basis of this that PVN chains are considerably more rigid than those of polystyrene. However the unperturbed dimensions of the molecules were not measured experimentally but were calculated from theoretical considerations.

In the present work an investigation has been made of PVN fractions in an ideal solvent.

POLYMER AND SOLVENT

As reported in [3] the original sample of PVN was separated into 13 fractions the greater part of which were used in the work cited. In order to obtain narrower fractions each 3–4 consecutive fractions were combined and refractionated. By this means 19 new fractions were obtained, 8 of which were used in the present work.

As the ideal solvent we used a mixture of toluene and decalin in the proportion of 1:1·3 (by weight), at a temperature of 30·2°C. The difference between the refractive indices of the two components was 0·013 which, with a total refractive-index gradient of PVN in admixture with the solvent of $dn/dc = 0{\cdot}176$, is quite admissible [4].

The solvents were purified by repeated redistillation *in vacuo*. Before measurement of light scattering the polymer solutions were freed from dust particles by

* Vysokomol. soedin. **2**: No. 2, 272–278, 1960.

centrifuging in special glass vessels with spring valves [5] in an acceleration field of 14,000 G. Dilution was carried out in the measuring cell. Before measurement of viscosity the solutions were filtered through a glass filter.

METHOD

The light scattering of the solutions was measured in a photoelectric nephelometer, described previously by one of the authors [6]. The wavelength of the light was 5460 Å. A cylindrical block of opalescent silicate glass was used as a working standard. For calibration of the latter the intensity of scatter of benzene at 20°, $I_0 = 1{\cdot}65 \times 10^{-5}$ cm^{-1} [7], was taken as the reference magnitude. The measurements were made by the well known dissymmetry method [8] which is quite satisfactory in an ideal solvent where the angle distribution function of scattering is undistorted [9, 10].

The characteristic values cH/I_{90}^i and $(Z\text{-}1)^{-1}$ (here H is the optical constant of the solution, c its concentration, I_{90}^i the excess intensity of scatter at 90° and ZI_{45}^i/I_{90}^i the dissymmetry of scatter of the solution) were determined graphically by extrapolating to $C=0$ the results of measurements, as a rule, at 8–10 concentrations. The calculations were made by means of the table given in reference [11].

The refractive index gradient, $dn/dc = 0{\cdot}176$, was measured at 30·2° in an IRF-23 refractometer with a differential prism.

The viscosity of the solutions was measured in an Ostwald viscometer. The efflux time of the solvent was 90·0 secs. The kinetic energy correction was small and was not introduced.

During measurement the solutions were placed in a thermostat with a precision of about 0·05°C. The thermostat and cell used in the photoelectric nephelometer were the same as those described for the visual, circular nephelometer [5].

RESULTS

The second virial coefficient for one of the PVN fractions was measured by light scattering at four temperatures.

The temperature at which $A_2 = 0$ (30·2°) was found by interpolation (Fig. 1).

Figure 2, a and b shows extrapolations to zero concentration of the values of cH/I_{90}^i and $(Z\text{-}1)^{-1}$ for all the fractions. The fact that these lines are parallel to the concentration axis confirms that the measurements were made under conditions such that the second virial coefficient A_2 of the solution was zero.

Experimental values for molecular weight M and values of the intrinsic dissymmetry of scatter, $[Z]$, obtained by means of Figure 2, a and b, are given in the second and fourth columns of the collated table. The root mean square distance $(\overline{h_0^2})^{1/2}$ between the ends of the clusters, for all the fractions, calculated from the intrinsic dissymmetry, $[Z]$, are given in the fifth column of Table 1.

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Experimental values of the viscosity of the solutions are shown in Fig. 2c, and values of the intrinsic viscosity of the fractions, $[\eta]_\omega$, are given in the third column of Table 1.

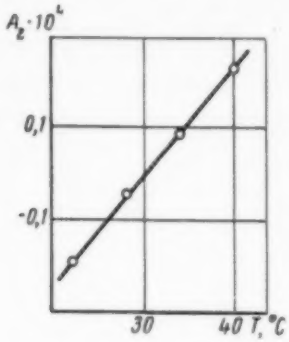

FIG. 1. Dependence on temperature of the second virial coefficient A_2 of PVN solutions.

DISCUSSION

The dependence of the intrinsic viscosity, $[\eta]_\omega$, of the fractions of PVN in an ideal solvent on molecular weight M is shown in Fig. 3, a on a double logarithmic scale.

The points for all the fractions, with the exception of that of lowest molecular weight, are a good fit to a straight line with a slope of 0·50. Consequently the relationship between $[\eta]_\omega$ and M takes the form

$$[\eta]_\omega = 5{\cdot}2 \times 10^{-4} M^{0{\cdot}65} \text{ dl/g} \tag{1}$$

Figure 3, b shows, on a double logarthmic scale, the dependence of the size of the molecules $(\overline{h^2})^{1/2}$ of the PVN fractions on molecular weight M in benzene [3] (dotted line) and in the ideal solvent (continuous line). The slope of the lines in both cases is 0·50. Thus both in benzene and in the ideal solvent the root mean square size of the PVN molecules (over the range of molecular weights investigated) is proportional to the square root of the molecular weight. Hence the distribution the molecules follows Gaussian statistics, undistorted by swelling of the molecules on passing from an ideal solvent to benzene. In view of the relationships [1]

$$(\overline{h_0^2})^{1/2} = CM^{0{\cdot}65} \tag{2}$$

and

$$(\overline{h^2})^{1/2} = \alpha \cdot (\overline{h_0^2})^{1/2} \tag{3}$$

for the size of the clusters in a good solvent $(\overline{h^2})^{1/2}$ and in an ideal solvent $(\overline{h_0^2})^{1/2}$, the Gaussian distribution of the molecular sizes in benzene means that the coef-

ficient of swelling of the molecules α must be independent of molecular weight. For the series of fractions used in reference [3] we determined the intrinsic viscosity in the ideal solvent, $[\eta]_\Theta$, and calculated α from the relationship [1]

$$\alpha = ([\eta]/[\eta]_\Theta)^{1/3} \tag{4}$$

where $[\eta]$ is the intrinsic viscosity in benzene. It was found, in fact, that over the molecular weight range corresponding to the points of the dotted line in Figure 3 b, α is practically independent weight (variation 1·16–1·24).

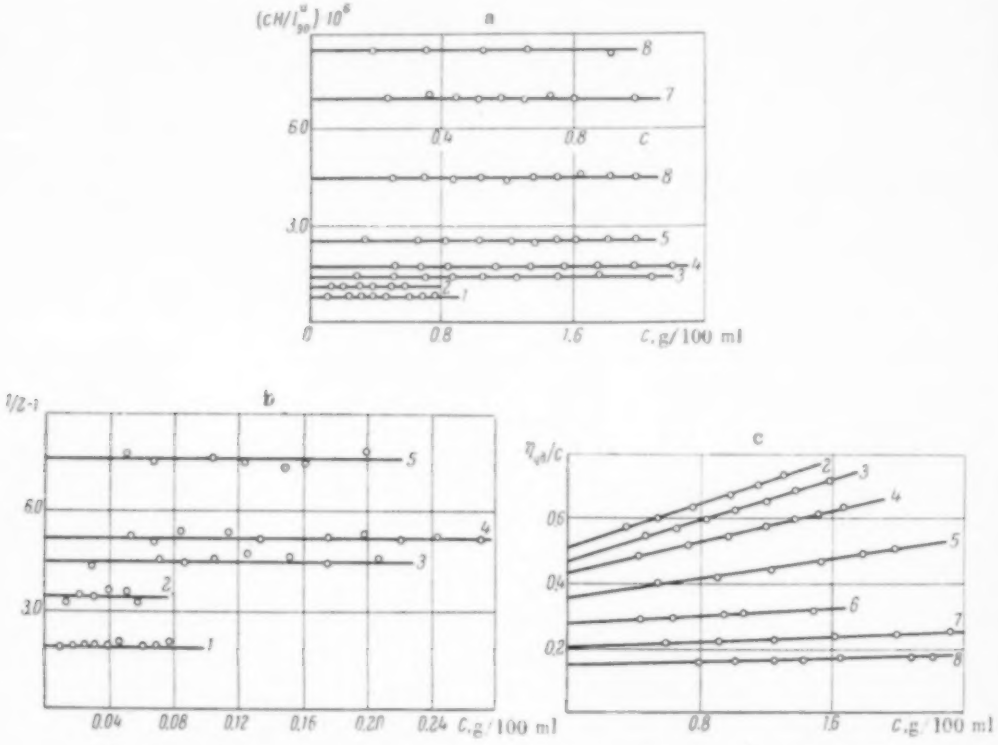

Fig. 2, a, b, c. Dependence on concentration, c, of the values of cH/I'_{90} (a); $(Z-1)^{-1}$(b); and η_{sp}/c (c).

At the same time it was found in the previous work [3] that the intrinsic viscosity of PVN in benzene, $[\eta]$, is proportional to $M^{0.8}$. For ordinary polymers (such as polystyrene), the molecular coils of which can be regarded as being non-draining solvent [1], the exponent 0·8 in the relationship $[\eta] \sim M^{0.8}$ corresponds to an exponent of 0·6 in the relationship $\overline{(h^2)}^{1/2} \sim M^{0.6}$ if we take into account that 1

$$[\eta] = KM^a \tag{5}$$

and $$(\overline{h^2})^{1/2} = C' M^{(1+a)/2} \quad (6)$$

Since for PVN in benzene $(\overline{h^2})^{1/2} \sim M^{0.5}$, the exponent 0·8 in $[\eta] \sim M^{0.8}$ must evidently be ascribed to partial draining of the PVN coils. Measurements of the coefficient of progressive diffusion D for PVN in benzene gave the relationship $D \sim M^{0.6}$, which is in agreement with the viscosity measurements and the supposition regarding the partial extension of the PVN molecules.*

TABLE 1. RESULTS OF MEASUREMENTS

Fraction No.	$M \cdot 10^{-6}$	$[\eta]$, dl/g	$[Z]$	$(\bar{h}_0^2)^{1/2}$ (A)	$(\bar{h}_{f.r.}^2)^{1/2}$ (Å)	$\left(\frac{\bar{h}_0^2}{\bar{h}_{f.r.}^2}\right)^{1/2}$	$\Phi \cdot 10^{-21}$
1	1·57	0·63	1·51	1030	312	3·3	0·91
2	1·00	0·50	1·29	790	250	3·2	1·00
3	0·78	0·46	1·23	700	220	3·2	1·00
4	0·64	0·42	1·19	640	198	3·2	1·00
5	0·43	0·35	1·13	540	163	3·3	0·96
6	0·24	0·27	1·08	400	120	3·3	1·00
7	0·16	0·20	—	—	—	—	—
8	0·12	0·14	—	—	—	—	—

Equation (6), which is true for unextended molecules, is not applicable to PVN in benzene. At the same time equation (6) is fulfilled for PVN in an ideal solvent where $a = 0{\cdot}5$.

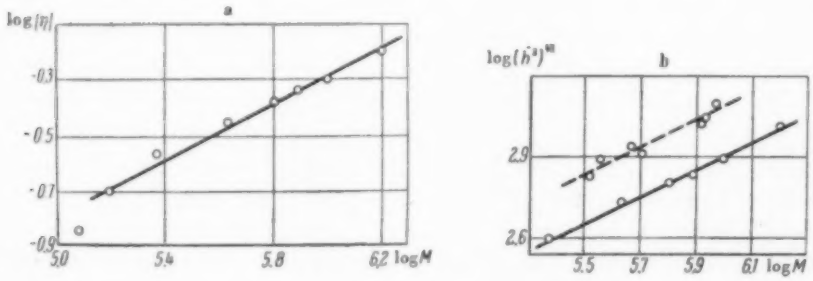

FIG. 3. a, b. Dependence of $\log[\eta]$ (a) and $\log(\overline{h^2})^{1/2}$ (b) on $\log M$ for PVN fractions in benzene (dotted line) and in the ideal (continuous line).

* The measurements of D were carried out by S. I. Klenin in the polymer solution laboratory of the Institute of Macromolecular Compounds, USSR Academy of Sciences.

Figure 3 b shows the following relationships for the size of the PVN molecules in benzene, $(\overline{h^2})^{1/2}$, and in the ideal solvent, $(\overline{h_0^2})^{1/2}$.

$$(\overline{h^2})^{1/2} = 1{\cdot}2 \times M^{0{\cdot}5}\,(\text{Å}) \tag{8}$$

and

$$(\overline{h_0^2})^{1/2} = 0{\cdot}81 \times M^{0{\cdot}5}\,(\text{Å}) \tag{9}$$

From (8) and (9) it follows that

$$\alpha = (\overline{h^2}/\overline{h_0^2})^{1/2} = 1{\cdot}5 \tag{10}$$

From the intrinsic viscosity in the same two solvents, mentioned above, it follows that

$$\alpha = ([\eta]/[\eta]_\Theta)^{1/3} \approx 1{\cdot}2 \tag{11}$$

It is seen that the values of the coefficient of swelling of the clusters, α, which are the same when calculated from (3) and (4) for ordinary, flexible polymer chains, are different for PVN. The reason for this is that on passing from an ideal to a good solvent the rotational friction of the PVN clusters (viscosity) increases to a considerably smaller extent than does their size.

The sixth column of Table 1 gives the root mean square size $(\overline{h_{f.r.}^2})^{1/2}$ of the PVN clusters calculated on the assumption of free rotation of all chain units, according to the relationship

$$(\overline{h_{f.r.}^2})^{1/2} = 3{\cdot}08\sqrt{p}\,(\text{Å}) \tag{12}$$

normally applied [1] to polyvinyl chains (p is the degree of polymerization)

The seventh column shows the ratio of the unperturbed size of the coils in an ideal solvent to that determined by free rotation of the units $(\overline{h_0^2}/\overline{h_{f.r.}^2})^{1/2}$. This ratio is accepted [1,2] as characteristic of the degree of flexibility of polymer chains. For polystyrene $(\overline{h_0^2}/\overline{h_{f.r.}^2})^{1/2} = 2{\cdot}3$ [12], for PVN we obtained $(\overline{h_0^2}/\overline{h_{f.r.}^2})^{1/2} = 3{\cdot}2$. For comparison this ratio is 1·8 for polyisobutylene and for the rigid chains of trinitrocellulose it is 4·2 [2].

Thus according to the relatively unperturbed dimensions of the coils, PVN occupies a position intermediate between polymers with flexible chains and those with rigid chains. However the rigidity of its chains still has no effect on their structural properties that are manifested in the angle distribution of light scattering, as is the case for a number of polymers with rigid chains [13, 14]. We found [3] that even in a good solvent, benzene, the angle distribution of scatter of PVN solutions does not show any substantial deviation from the classical Debye plot. From these considerations it seems to us that the PVN macromolecules should be assigned to the class of semi-rigid chains, the hydrodynamic behaviour of which requires special theoretical consideration.

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In the previous paper [3] we calculated $(\overline{h_0^2}/\overline{h_{f.r.}^2})^{1/2}$ for PVN from measurements in benzene using the theoretical relationship from references [15] and [16]. By this means we obtained a mean value of 4·6 instead of 3·2–3·3 (by direct measurement in the ideal solvent). This shows that the relationships that we used between $[\eta]$, $[\eta]_\Theta$, Φ, A_2 and M from the papers cited, are not applicable to semi-rigid chains of anomalous hydrodynamic behaviour. Calculation of the unperturbed size of the coils, $(\overline{h_0^2})^{1/2}$, from the intrinsic viscosity in an ideal solvent, $[\eta]_\Theta$, from the relationship

$$[\eta]_\Theta = \Phi \frac{(\overline{h_0^2})^{3/2}}{M} \tag{11'}$$

can also not be made with a value of Φ for flexible polymeric chains.

The constant k in the viscosity equation

$$\eta_{sp}/c = [\eta] + k[\eta]^2 c \tag{12'}$$

for fractions of PVN in the ideal solvent has the value 0·5–0·8, which is usual for molecular chains in an ideal solvent [17, 18].

The anomalous hydrodynamic properties of the semi-rigid PVN chains, mentioned above, must be related to a small value of the constant, Φ, in Flory's equation [1]:

$$[\eta] = \Phi \frac{(\overline{h^2})^{3/2}}{M} \tag{13}$$

not only in a good, but also in an ideal solvent. The eighth column of Table 1 shows that Φ for PVN in the ideal solvent is $\approx 1 \times 10^{21}$ instead of 2×10^{21} for polymers with flexible chains (the theoretical value, $\Phi = 2{\cdot}8 \times 10^{21}$, is still higher). Hence it follows that the friction of a semi-rigid macromolecule, in viscous flow of the solution, increases considerably more slowly than its dimensions (in comparison with a flexible macromolecule of the same degree of polymerization). The cause of this seems to us to lie in the specific structural features, in particular in some geometric asymmetry of a semi-rigid macromolecule. Tsvetkov and Shtennikova found that the asymmetry of ethylcellulose in solution is considerably greater than in polymers with flexible chains (from the magnitude of the shape effect in streaming birefringence). At the same time it is known that the exponent a in equation (5) has a high value ($\approx 1{\cdot}0$) for derivatives of cellulose [19], resulting from a high degree of extension of the rigid, brittle clusters.

On passing to a good solvent (benzene) the size of the PVN clusters increases 1·5 times and the value of Φ decreases to $\approx 0.5 \times 10^{21}$ [3]. In these circumstances clusters that are not extended in a solvent ($[\eta]_\Theta \sim M^{0.5}$) become partially extended ($[\eta] \sim M^{0.8}$). We see therefore that in both an ideal and a good solvent the semi-rigid PVN clusters display unusual hydrodynamic properties, for the full explanation of which further experimental material is necessary (streaming birefringence, diffusion in an ideal solvent, sedimentation), as well as a special theoretical treatment of the problem.

In conclusion the authors cordially thank V. N. Tsvetkov for his interest in this work and O. B. Ptitsyn for very profitable discussion.

CONCLUSIONS

(1) The light scattering and viscosity of eight fractions of PVN in an ideal solvent ($A_2=0$) have been measured. The molecular weight of the fractions and the mean size of the clusters in solution have been determined.

(2) The imperturbed dimensions of the PVM clusters is 1·4 times greater than those of polystyrene of the same degree of polymerization. Thus substitution of the benzene rings in the side groups of the polystyrene chain by the naphthalene bicyclic structure considerably increases the thermodynamic rigidity of the macromolecule.

(3) Comparison of the dimensions of the clusters and intrinsic viscosity of PVN in benzene and in an ideal solvent indicates unusual hydrodynamic properties for the semi-rigid chains of polyvinylnaphthalene.

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POLYDIMETHYLPOLYPHENYLSILOXANES BY CATALYTIC CONDENSATION*

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THE technical use of organosilicon polymers has brought about the necessity of investigating their properties at high temperatures. The properties of polydimethylpolyphenylsiloxane (L), obtained by catalytic polymerization from phenyltrichlorosilane and dimethyldichlorosilane, are described in this paper. Polymer II contained 25 per cent more trifunctional monomer than I. Polymer III differed from I in containing 5 per cent of a tetrafunctional component; polymer IV differed from polymer II in the same way. Polymer V contained polyaluminomethylphenylsiloxane. Investigation of the properties was carried out on the free films and on films on a metal substrate.

Experiment has shown that the mechanical properties of polymer films depends on their composition and they vary markedly with temperature. Polymer II, containing more of the trifunctional monomer, is rather stronger at room temperature than I but the strength of both polymers falls sharply with increasing temperature (Fig. 1, curves I and II). The introduction of 5 per cent of a tetrafunctional crosslinking agent increases the initial mechanical strength a little (polymer III), lowers the elongation in the original state from 40–50 to 15 per cent and increases it to 60–70 per cent at high temperatures. The mechanical strength falls considerably more slowly with increase in temperature (curve III).

The introduction of a crosslinking agent with polymer II results in a decrease in the elongation at break from 20 to 10 per cent in the original state, and at 160–180 the elongation is 60–70 per cent. The mechanical strength of polymer IV falls considerably less with increasing temperature than does that of the original polymer II. The addition of polyaluminomethylphenylsiloxanes reduces still further the effect of temperature on mechanical strength (curve V). The elongation at break does not exceed 15–20 per cent.

Figure 2 shows the thermomechanical properties of these polymers. The curves indicate that polymer II has a higher glass temperature (T_g) than polymer I. The glass temperatures of polymers III–V are also higher. The deformations found in the study of the thermomechanical properties are in complete agreement

* Vysokomol. soedin. **2**: No. 2, 279–283, 1960.

with the results of the mechanical investigation. The largest deformation is observed in polymer I. Polymer II, containing more trifunctional groups, has a smaller deformation. The introduction of a tetrafunctional crosslinking agent (polymer III) leads to an increase in T_g in comparison with I and to a decrease in deformation. The high-elastic deformation is decreased still further in polymer V, which contains polyaluminomethylphenylsiloxane.

The thermomechanical curves of the polyorganosiloxanes I–V differ markedly from the general form, particularly at high temperatures. Polymer II manifests flow at 320° and polymer I above 400°C. Polymers III and V do not show flow up to 550°C. Deformation is considerably reduced in polymers I and III above 300°C. This is evidently the result of crosslinking.

The specific feature of the thermomechanical properties of polyorganosiloxanes that distinguishes them from organic polymers is the lowering of high-elastic deformation with increase in temperature.

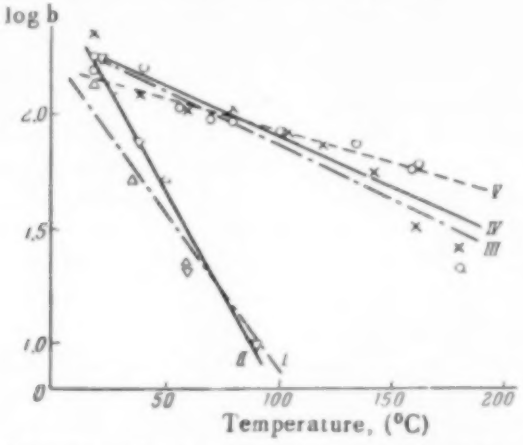

FIG. 1. Dependence of mechanical strength of polymers I–V on temperature. The numbers on the straight-line plots are the polymer numbers.

The decrease in deformation at high temperatures in the high-elastic region is explained by the fact that the viscosity of polyorganosiloxanes changes with temperature considerably less than that of organic polymers [1].

Viscous flow begins to have an effect on the thermomechanical properties in the high-elastic region. This effect takes the form of irreversible deformation which is greater nearer to the softening point and increases with time of heating. Thus plastic deformation always occurs in addition to high-elastic deformation. High-elastic deformation must decrease with increasing temperature because of the inevitable increase in the high-elastic modulus. For organic polymers this decrease is masked by the increase in plastic deformation. In polyorganosiloxanes, because of the lower temperature-dependence of viscosity their plastic deformation is less and it does not mask the decrease in high-elastic deformation.

In order to examine the effect of crosslinking at high temperatures the polymers were heated for 24 and 72 hours at 250° (curves 2 and 3, Fig. 3, a, b, c, d; curve 1 corresponds to the unheated sample). Heating polymer I at 250° leads to an increase in T_g and a decrease in high-elastic deformation, indicating an

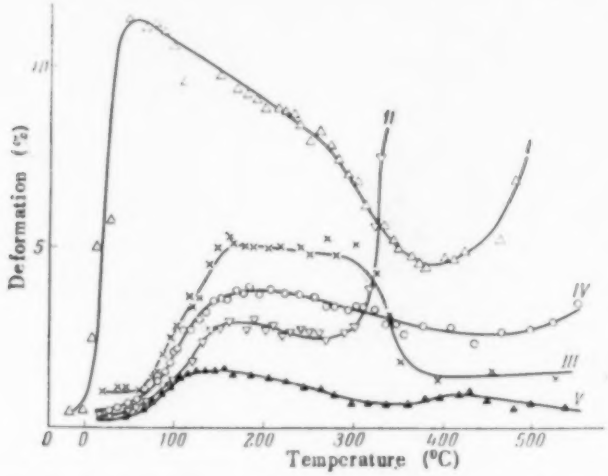

FIG. 2. Thermomechanical properties of polymers I–V. The numbers on the curves are the polymer numbers.

increase in the number of crosslinks, i.e. that network formation is taking place. The glass temperature, T_g, of polymer II rises after heating and the deformation decreases, while the flow temperature (T_f) remains unchanged. It would be expected that polymers I and II, obtained from di- and trifunctional monomers, would have a crosslinked structure and would not exhibit flow. However this is not borne out by experiment. Both polymers, I and II, pass at high temperatures to the viscous-flow state.

TABLE 1. ABSORPTION OF BENZENE VAPOUR BY THE POLYMER FILMS AT 20° (IN % OF FILM WEIGHT)

Polymer	Duration of heat treatment at 250°C (hr)			
	0	1	3	21
I	107	60	66	72
II	115	72	64	59
III	88	52	63	67
IV	85	62	57	66

Investigation of the action of solvents on polymers I and II showed that they swell over benzene at 20°, absorbing about 110% of the vapour, and the

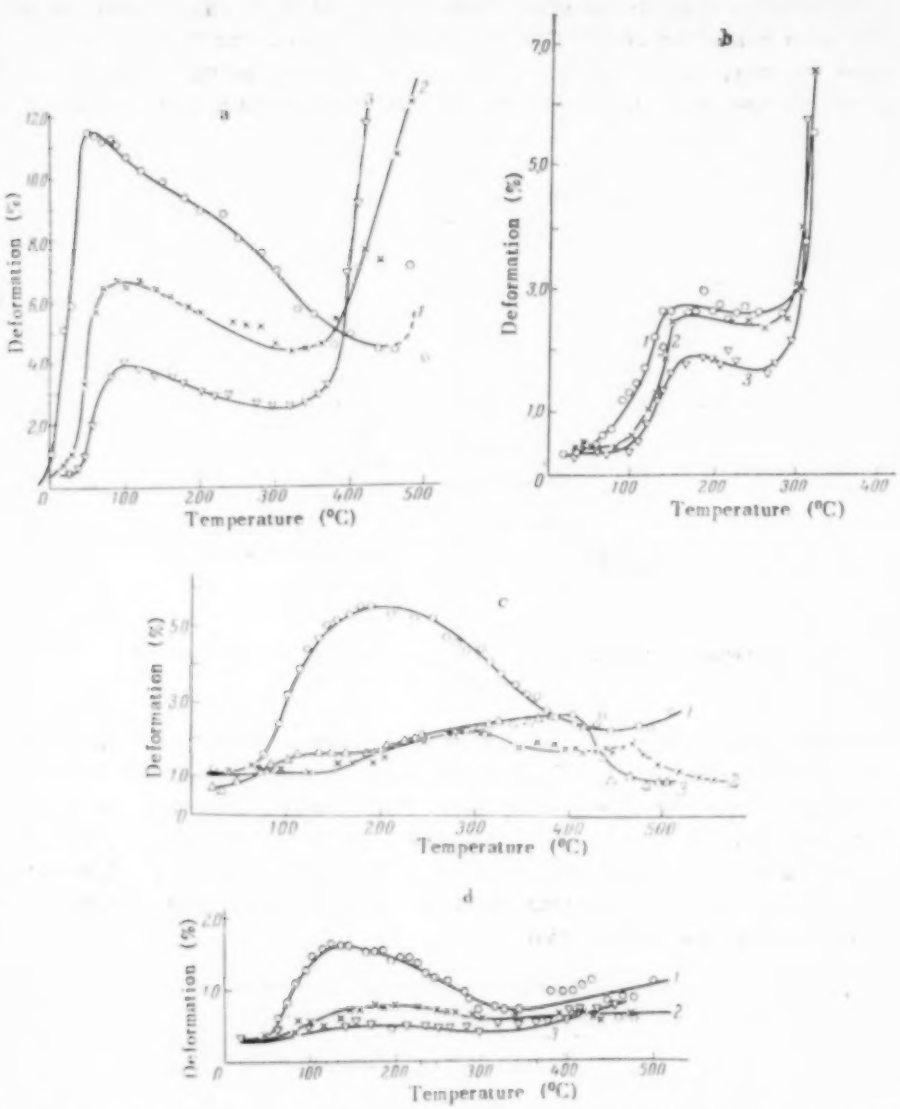

FIG. 3. Dependence of thermomechanical properties on duration of heat treatment: (a) polymer I, (b) polymer II, (c) polymer IV, (d) polymer V; (1) unheated sample; (2) heated 24 hours at 250°; (3) heated 72 hours at 250°C.

mechanical strength thereupon falls from 130–150 to 0·3 kg/cm² in the case of polymer I and from 170 to 0·2 kg/cm² for polymer II. These results indicate that the molecules of these polymers have a cyclo-linear structure with a large number of branches [2,3].

Polymers III, IV and V, containing tetrafunctional monomers, change their structure on heat treatment such that they no longer show significant high-elastic deformation and do not flow up to 550° (Fig. 3, c and d, curves 2 and 3). These polymers are less swollen by benzene (Table 1).

The temperature-frequency dependence of dielectric permeability and the tangent of the loss angle were determined for polymers I–V. The investigations

TABLE 2. VALUES OF ε_0^1 AND TAN δ OF THE POLYMERS

Polymer	ε_0^1 at 20°	tan δ at 20° x 10^3	Maximal value of tan δ 10^2
I	3·7	0·51	0·76
II	3·2	0·34	0·47
III	3·4	0·24	0·27
IV	3·5	0·26	0·34
V	3·2	0·25	—

were carried out over the frequency range of $100–1·5 \times 10^6$ hertz and at temperatures from −50 to 200°C. The variation in dielectric permeability and tangent of the loss angle of polymers I–IV in this temperature range involves a dipole-elastic mechanism [4]. This variation is most marked in polymer I in the temperature region from 35 to 50° and in polymer II in the region 50–65° but here it is less pronounced, and in polymers III and IV this variation is barely noticeable in the temperature region of 50–80°C. In polymer V the dielectric permeability does not change up to 120° and above 120° it falls gradually. Values of the dielectric permeability and tangent of the loss angle are given in Table 2, for frequency of 1,000 hertz and a temperature of 20°C. With an increase in the number of crosslinks the high-elastic deformation falls and at the same time the effect of relaxation changes on the electrical properties of the polymer decreases. For polymer I the relaxation change in the dielectric permeability is 2·6 per cent, for polymer II 1·5 per cent and for polymers III and IV about 1 per cent. This can be seen from the variation in the value of the tangent of the loss angle from that at 20° to its maximal value determined by the dipole-elastic loss (Table 2).

CONCLUSIONS

(1) Polydimethylpolyphenylsiloxanes, prepared by the co-hydrolysis of phenyltrichlorosilane and dimethyldichlorosilane do not have a crosslinked structure. On investigation of their thermomechanical properties these polymers exhibited flow at high temperatures.

(2) The introduction of tetrafunctional monomers into the above polymers leads to an increase in mechanical strength in the high-elastic state, to a widening of the region of high-elasticity and to crosslinking of the polymer.

(3) In the polydimethylpolyphenylsiloxanes changes in the dielectric permeability and tangent of the loss angle involve a dipole-elastic mechanism.

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THE PRODUCTION OF ISOTACTIC POLYMETHYLMETHACRYLATE BY POLYMERIZATION OF THE FROZEN MONOMER*

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IN previous papers [1, 2] it was reported that methyl methacrylate (MMA), as well as a number of other monomers, can be polymerized in the solid state by condensation, together with magnesium, on to a surface cooled by liquid nitrogen. Polymerization begins in the frozen molecular mixture at a temperature in the region of −100 to −110°, i.e. considerably below the melting point of MMA (−50°), and proceeds at a high rate (under conditions of poor heat transfer even at an explosive rate). When investigating the properties of polymethylmethacrylate (PMMA) prepared in this way, we found that it was a homogeneous polymer and did not contain free magnesium. The quantity of combined magnesium calculated from the ash content did not exceed 0·5 per cent by weight in any sample. The polymer forms transparent solutions in toluene and dichloroethane and still contained combined magnesium after reprecipitation.

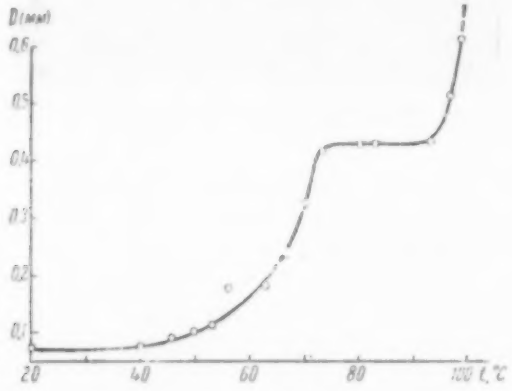

FIG. 1. Thermomechanical curve of PMMA sample. Load, 83 g/mm².

Part of the polymer did not go into solution and remained in the form of a transparent mass. The intrinsic viscosity of the fraction soluble in dichloroethane was 0·3.

* Vysokomol. soedin. **2**, No. 2, 303–305, 1960.

Figure 1 shows the thermomechanical curve of one of these polymer samples. It is seen that its softening temperature is about 50°C. The density of the sample determined in a density-gradient tube was $d^{20} = 1{\cdot}233$ g/cm³. (The softening point of PMMA obtained by ordinary radical polymerization is 90–105° and the density $d^{20} = 1{\cdot}20$ g/cm³). The polymer obtained in this way crystallizes after swelling in heptan-2-one. The X-ray diffraction pattern of the crystallized PMMA sample is shown in Fig. 2. The properties of this polymer practically coincide with those of isotactic PMMA prepared by polymerization of MMA by lithium alkyls in non-polar media [3, 4]. This gives grounds for assuming that our PMMA

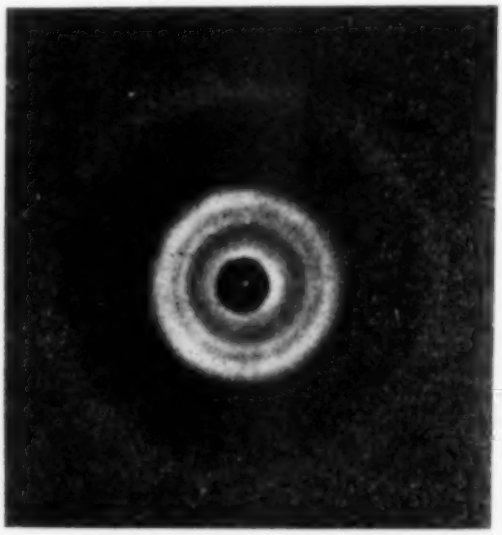

FIG. 2. X-ray diffraction pattern of crystallized PMMA sample.

also has an isotactic structure. (The properties of syndiotactic PMMA are quite different from those of the isotactic material. Its softening point is 115–135° and density 1·18–1·19 g/cm³ [3,4]) *.

In reference [2] we put forward the suggestion that polymerization in solid, molecular mixtures, obtained by the simultaneous condensation of monomer and Mg vapours, is initiated by radicals of the type $Mg-CH_2-CH-R$, formed in the gas phase by the interaction of "hot" Mg atoms and monomer molecules. The radical nature of the process was confirmed by an electron paramagnetic resonance study [2] of polymerization in the analogous system, acrylonitrile-Mg. At the same time Fox *et al.* [3,5] have shown that in the low-temperature, homogenous, radical polymerization of MMA in the unfrozen state, only syndiotactic

* As has already been pointed out by Korotkov and co-workers [4], the isotactic structure was erroneously ascribed to syndiotactic PMMA by Fox *et al.* [3].

polymer can be obtained. This results from the fact that under these conditions the free energy of activation of the alternate addition of monomer molecules in the syndio position is lower than that in the iso position. Hence at sufficiently low temperatures the energy conditions more favourable to the syndiotactic configuration are rigidly selected.

Evidently in the low-temperature polymerization of frozen MMA in the system produced by the method of molecular packing, the already existing state of order in the frozen monomer phase has a profound effect on the thermodynamic parameters of the chain growth reaction. In other words the nature of the packing of the monomer molecules in the solid phase favours the formation of polymer chains with an isotactic structure.

CONCLUSIONS

In this work it was found that on polymerization of methyl methacrylate in a frozen system, obtained by the simultaneous condensation of the monomer vapour with that of metallic magnesium, isotactic polymethylmethacrylate is formed.

It has also been shown that the preliminary ordering of the monomer molecules in the solid phase has an effect on the formation of the structure of the polymer chains.

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ULTRAVIOLET ABSORPTION SPECTRA OF CARBANIONS IN THE POLYMERIZATION OF STYRENE IN THE PRESENCE OF ORGANOMETALLIC COMPOUNDS*

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INVESTIGATIONS of polymerization and copolymerization in the presence of organic compounds of the alkali metals has shown that the composition of the copolymers and the structure of the polymer chain depends on the nature of the alkali metal and of the medium [1–4]. For example the composition of a number of copolymers changes considerably in passing from sodium to lithium organic compounds and also on substituting amine or ether media by hydrocarbon solvents.

These results are explained by the increase in polarity of the bond in passing from LiR to NaR. The special features of polymerization in the presence of organolithium compounds is regarded as resulting from the fact that because of the relatively low polarity of the LiR bond the lithium component of the catalyst, as well as the carbanion, plays a significant rôle in the acts of chain growth. This effect is particularly marked in pairs of monomers, one component of which contains two conjugated double bonds one of which reacts preferentially with the lithium and the other with the carbanion component of the catalyst. Under typical anionic polymerization conditions (for example in the presence of NaR in ether) chain growth is determined only by interaction of the monomer and the carbanion and consequently the reactivity of the monomer is controlled only by its properties as an electron acceptor.

Investigation of the kinetics of polymerization of styrene in the presence of organolithium compounds has shown that the rate of polymerization increases sharply on substituting hydrocarbon solvents by an amine, an ether or tetrahydrofuran, and also on changing from LiR to NaR [1, 4, 5]. Even in polar media the rate of polymerization of styrene in the presence of NaR was considerably higher than that with LiR. It follows therefore that the structure of the carbanion component of the catalyst (the distribution of the electron cloud, the magnitude of the excess charge) is different for LiR and NaR, not only

* Vysokomol. soedin. **2**: No. 2, 310–312, 1960.

in hydrocarbons but also in polar solvents. It seemed of interest to verify this conclusion concerning the different structure of the carbanion in different circumstances, not only kinetically but also by other methods.

As is known, the conversion of a compound of the aliphatic substituted aromatic series to the corresponding carbanion of the benzyl type leads to a shift in the absorption band in the long-wave region of the spectrum and to the appearance of colour. In view of this we examined the ultraviolet absorption spectra of the carbanions formed during the polymerization of styrene in the presence of organolithium compounds and sodium at room temperature in different media. On polymerization of styrene under these conditions so-called "living" polymers are formed, with coloured, benzyl-type carbanions at the ends of the polymer chains.

Measurement of the optical density D of the solutions was carried out in a quartz cell (absorbing layer 2 mm) in an SF-4 spectrophotometer, by a method similar to that described by Astaf'ev [6]. The cell was filled with the solution to be examined, under conditions that excluded contact with moisture and oxygen. The purification of the starting materials was described in an earlier paper [4]. Because of the interaction of tetrahydrofuran and lithium alkyls this solvent was added to the system after polymerization of the styrene for investigation of the spectra of the carbanions in this medium.

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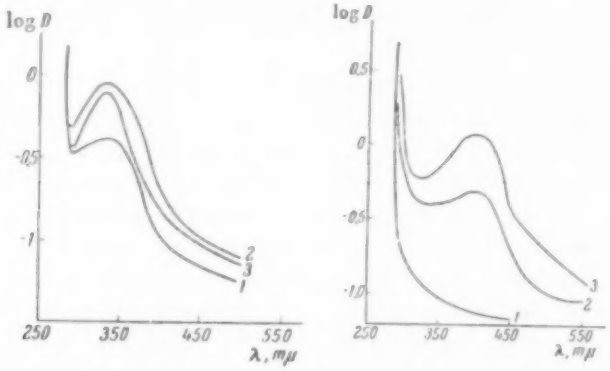

FIG. 1. Dependence of optical density on λ. (a) For lithium-polystyrene in different media: (1) toluene; (2) 70% toluene, 30% triethylamine; (3) 80% toluene, 20% tetrahydrofuran. (b) For the solvent (1) and sodium-polystyrene in different media: (1) 70% toluene, 30% triethylamine; (2) toluene; (3) 70% toluene, 30% triethylamine.

In view of the transparency of the solvent in the region studied (Fig. 1b, curve 1) the optical density of the solution was determined in relation to the optical density of air at a carbanion concentration below 10^{-3} moles/litre. The dependence of log D on the wavelength λ was determined for each solution in

order to assess λ_{max}, the region of maximal absorption for the given system. The results obtained are shown in Fig. 1a and b, and in Table 1.

Table 1. The dependence of λ_{max} of polystyrene carbanions on the nature of the alkali metal and the medium.

Cation	Medium	λ_{max} (mμ)
—	Toluene (70%) + triethylamine (30%)	—
Li	Toluene	330
Li	Toluene (70%) + triethylamine (30%)	330
Li	Toluene (80%) + tetrahydrofuran (20%)	330
Na*	Toluene	395
Na*	Toluene (70%) + triethylamine (30%)	395

* In these systems the carbanion solutions were examined under conditions that excluded the presence of metallic sodium.

The results show that the change from the compound LiR to NaR (where R is the polystyrene carbanion) brings about a shift in the ultraviolet spectra toward the long wave side. The region of maximal absorption for NaR is close to that for the free benzyl carbanion (see the data calculated from the literature in the survey [6]). A change in the medium (the change from hydrocarbon solvents to an amine and tetrahydrofuran) does not affect the position of the ultraviolet absorption band of the system studied but it causes an increase in the intensity of absorption in this region.

As stated above, the conversion of aliphatic substituted aromatic compounds to benzyl-type carbanions causes a shift in the ultraviolet absorption maximum toward the long wave side. In accordance with this it may be thought that the increase in the carbanionic character of the component R in MeR, brought about by the substitution of lithium by sodium in the corresponding organic compounds, or a change in the medium by the introduction of an electron-donor material can also lead to a shift in λ_{max} toward the longer wave side. As the results show, on passing from lithium to sodium organic compounds a shift in the region of maximum absorption toward the longer wave side is in fact observed. However the addition of an amine or tetrahydrofuran has no effect on the position of the absorption maximum in the ultraviolet spectra of these systems.

For further elucidation of the structural features of the carbanions of polystyrene in relation to the conditions, an investigation of these compounds will be carried out in the future by infrared spectroscopy and by other physical methods.

CONCLUSIONS

(1) On passing from lithium to sodium organic compounds in the polymerization of styrene the region of maximal absorption in the ultraviolet spectra shifts toward the longer wave side. The movement observed is in accord with

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the view that this is connected with the increase in the carbanionic character of the component R in the compound MeR on substituting lithium by sodium in corresponding organic compounds.

(2) A change in the nature of the solvent has no effect on the position of the absorption maximum in the ultraviolet spectra, it only alters the intensity of absorption.

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THE RHEOLOGICAL PROPERTIES OF CONCENTRATED POLYMER SOLUTIONS*

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THE crystalline and high-elastic states of polymers are the typical and in many respects the extreme states. They make possible the preparation on the one hand of suspensions and pastes, consisting of two-phase systems that are closely related to systems with a crystalline disperse phase formed by a crystalline, low-molecular compound. On the other hand rubber-like polymers form solutions with properties characteristic of elastic liquids. It is characteristic of highly concentrated pastes (pseudogels) that intensive relaxation processes take place in them only under rather high shear stresses. On the other hand in non-Newtonian-elastic and nonelastic liquids (solutions) relaxation processes occur fairly rapidly even under very low shear stresses. The question naturally arises, to what extent is the transition from one extreme to the other continuous? In this connexion a rheological investigation of a system of intermediate type, occupying a position between the above systems, is of considerable interest, the more so because this problem has not received attention until recently and it has not so far been studied. Concentrated solutions of polymers with fairly rigid macromolecules in solvents that from the rheological point of view border on poor solvents, are worthy of attention in this connexion.

Ideas on good and poor solvents are essentially different for polymers with flexible (such as rubber) and with rigid macromolecules (such as cellulose and its esters). In the case of flexible macromolecules the solutions formed in good solvents are more viscous than those in poor solvents. The reverse is true for the cellulose ester type of polymer. Here good solvents give less viscous solutions. It should be noted that this classification of polymer-solvent systems, which is very important in relation to rheology, remains essentially undeveloped.

In this work solutions of ethyl cellulose in methylcellosolve (ethylene glycol monomethyl ether) were studied. Unfractionated, grade "K" ethyl cellulose with an ethoxyl number of 46 was used. Methylcellosolve is a commercial product (b.p. 120°; d_{20} 0·96 and η_{20} 1·8 centipoise).

The rheological properties of the solutions were studied with a Pavlov rotational elastoviscometer [1] under conditions of practically uniform stress (the

* Vysokomol. soedin. **2**: No. 3, 329–336, 1960.

variation in apparent stress during operation did not exceed 8 per cent) and in a constant-head capillary viscometer [2]. The elastic-strength and viscosity properties were studied with ethyl cellulose solutions in a concentration range of 5 to 20 g per 100 ml of solvent, at temperatures from −20 to 80°C.

The ethyl cellulose solutions were always made homogeneous. To accelerate solution of the ethyl cellulose the solutions were stirred mechanically with a propellor-type stirrer, for several hours. They were then de-aerated by holding them at 90° for 4–5 hours and filtered at 80° under pressure through two layers of fine metal gauze and four layers of filter paper. De-aeration and filtration

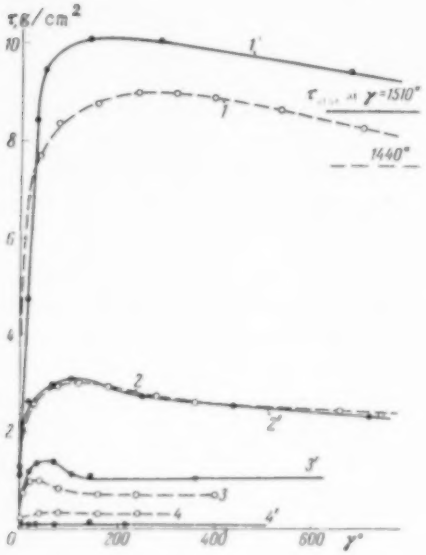

FIG. 1. Dependence of shear stress on deformation at a rate of deformation of 1·61 sec^{-1}, for ethylcellulose solutions. Dotted curves—solutions of different concentrations at 20°: (1) 20; (2) 15; (3) 10; (4) 8 g/100 ml. Continuous curves—15% solution at different temperatures: (1′) −20°; (2′) −20°; (3′) 50°; (4′) 80°C.

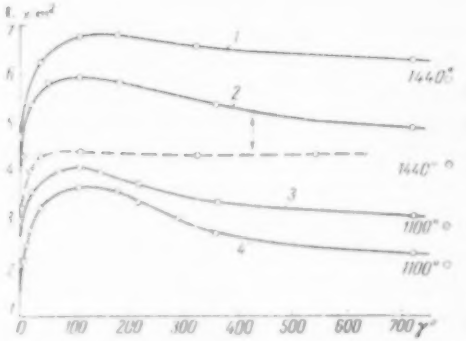

FIG. 2. Dependence of shear stress on deformation for a 15% solution of ethylcellulose at 20° and various rates of deformation. Dotted curves—repeat tests on the system. (1) D=12·75; (2) 5·3; (3) 2·55; (4) 0·51 sec^{-1}.

were carried out on the day in which the solutions were prepared and the rheological examination took place four days later.

Figure 1 shows the dependence of the shear stress (τ) in the sample, on the angle of rotation (γ°) of the cylinders of the rotational elastoviscometer, at a rate of deformation of D=1·61 sec^{-1} (corresponding to the deformation-flow regime set up), with a torsion wire of modulus c=0·46 g cm degree^{-1}. The shape of the

$\tau(\gamma)$ curves indicates that these systems at concentrations from 10% and upwards, and at temperatures below 50°, have a clearly defined yield value (τ_f) corresponding to the maximum on these curves. Near the upper curves in Figure 1 are shown the angles of rotation of the inner cylinder of the elastoviscometer at which a stationary regime of flow of the system is reached (corresponding to a shear stress $\tau_{stat.}$). The dependence of τ_f on concentration, c, and absolute temperature is expressed by an exponential function of the form $\tau_f = me^{ac} = ne^{-bT}$, where a,b,m and n are constants.

The ratio $\tau_f/\tau_{stat.}$ with increasing temperature from −20 to 80° increases from a value of 1·2, reaches a maximum of about 1·4 and then falls to unity. At 20° for a 10% solution this ratio is 1·3 and for a 10% solution it is 1·9.

Figure 2 shows curves of $\tau(\gamma)$ at various values of D for a 6 per cent solution at 20°. For a 25-fold variation in D, τ_f changes by a factor of 1·9. This order of variation in gel properties with change in rate of deformation characterizes the system as one occupying a position intermediate between plastic pseudogels and non-Newtonian liquids. In fact, in the case of pseudogels of the type of lubricating greases the structural framework, formed by crystals, is rather rigid and of low elasticity [3], consequently τ_f varies little with D. The values of τ_f vary by only a few times for a change in D of many orders. On the other hand for elastic, non-Newtonian liquids (solutions of aluminium naphthenates in hydrocarbon media) the maximum in the $\tau(\gamma)$ curves varies very markedly with D [4]. The ratio $\tau_f/\tau_{stat.}$ falls sharply with increasing D (from 1·8 at $D=0{\cdot}51$ sec^{-1} to 1·2 at $D=1{\cdot}2$ sec^{-1}). This places the systems in question in the same series as pseudogels, for which a sharp fall in this ratio is typical. On re-testing these samples no maxima in the $\tau(\gamma)$ curves were observed (dotted curve 2, Fig. 2). However, with the passage of time, as a result of relaxation of the systems, the original properties are restored.

The existence of yield values for concentrated solutions of ethylcellulose—maxima in the $\tau(\gamma)$ curves—before which they exhibit the properties of a solid body, is connected with the fact that as a result of interaction between the rigid macromolecules a fairly strong, three-dimensional framework is formed. With an increase in concentration the rigidity of the macromolecules and the bond energy of the structural framework formed increase, thus increasing the gel strength. A decrease in temperature, by decreasing the energy of thermal movement, increases the degree of association and rigidity of the macromolecules, and also brings about an increase in τ_f. On passing through the yield value and reaching steady flow the structural framework breaks down, orientation of the macromolecules occurs with packing in the direction of flow [5].

Let us turn to an examination of the viscosity properties of ethylcellulose solutions. On Fig. 3a are shown, on a double logarithmic scale, characteristic flow curves, obtained with the rotational elastoviscometer of solutions of various concentrations at 20°, and on Fig. 4 of a 15% solution at various tempera-

tures. Here and in subsequent diagrams D is given as usual in sec^{-1}, τ in dynes/cm^2 and η in poises. Curves 1 in Fig. 3 and 4 were obtained with freshly-prepared samples, not previously subjected to testing, passing from low to higher values of D successively. Curves 2 and 3 correspond to samples subjected to higher and lower D respectively. Curves 2 and 3 can be traversed in either direction. On curve 2 this is shown by two arrows directed toward both higher and lower D. Although curve 3 has only one arrow, corresponding to the regime under

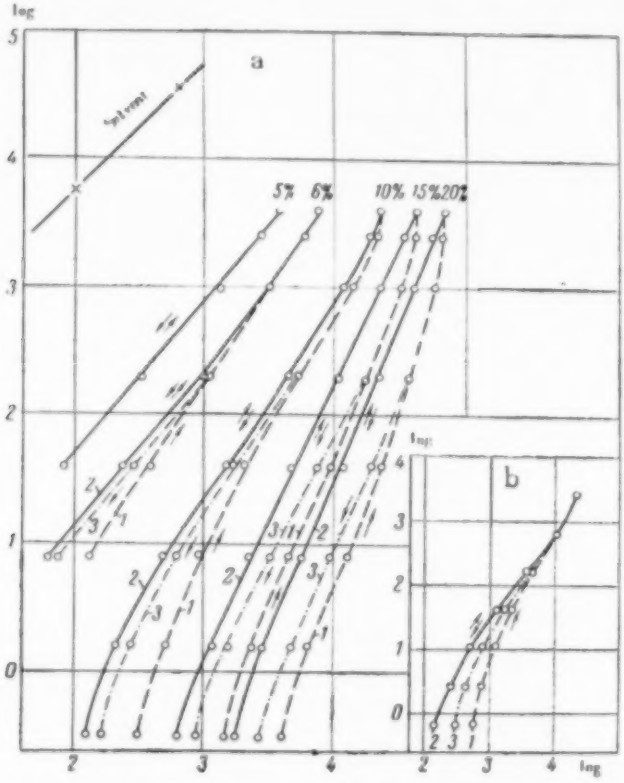

FIG. 3. Characteristic flow curves of ethylcellulose solutions. (a) Solutions of different concentrations at 20°; (b) 10% solution at 20°.

which the test was conducted, control experiments showed that it also can be traversed not only in the direction of decreasing, but also of increasing D. Fig. 3b shows, by the example of a 10 per cent sample, the thixotropic restoration of the viscosity properties of the solutions after relaxation. Here curve 3 was obtained after curve 2 and after keeping the system at rest for 24 hr.

It is seen from Fig. 3 and 4 that an increase in concentration has an effect on the viscosity properties of the solution similar to that of a decrease in temperature.

Under the action of a rate gradient in viscous flow partial breakdown of the spatial structure of the dissolved polymer takes place and the mean, statistical size of the clusters of the rigid, polymer molecules decreases [6]. In addition to this, partial breakdown of the structural framework orientation of the macromolecules in the direction of flow occurs [5]. The degree of orientation in the direction of flow and the breakdown of the original spatial arrangement increase with increasing D.

The viscosity properties of ethylcellulose solutions vary in a complex manner with temperature, depending on the interaction of the macromolecules with

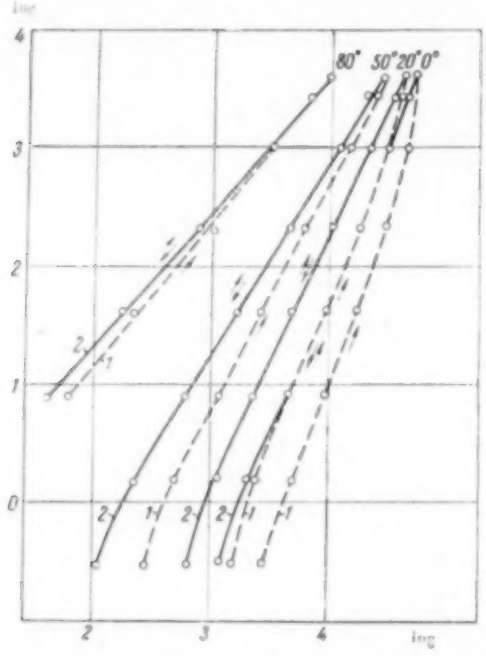

FIG. 4. Characteristic flow curves of a 15% ethylcellulose solution at various temperatures; denotations as for Fig. 3.

the solvent and on the temperature dependence of the viscosity of the solvent Figure 5 shows, on a double logarithmic scale, curves characterizing the dependence of the effective and relative effective viscosities (η_{ef} and $\eta_{rel} = \eta_{ef}/\eta_0^1$, where η_0^1 is the viscosity of the solvent) on D, for a 15 per cent solution at various temperatures. Examination of these curves shows that η_{ef} and η_{rel} decrease with increasing temperature. The decrease in the thickening effect of the polymer with increasing temperature has a decisive effect on η_{ef}. The effect of temperature on the viscosity properties of these solutions increases with their degree of structure formation. In solutions with a weaker or partially degraded structure

the variation of viscosity with temperature is less. It is seen from Fig. 5 that in the region of high D the effect of temperature on the viscosity of the solutions is in fact lower. The decrease in η_{rel} with increasing temperature in these systems establishes their essential difference from typical pseudogels, in which η_{rel} increases with increasing temperature [8].

In viscous flow the macromolecular aggregates that form the structural framework of the systems are subjected not only to rupture but also to forced contact, the exent of which increases with increasing t° and c. The strength of the structural framework under static conditions and the viscosity of the systems after relaxation are determined by the most favourable mutual disposition of the macromolecules, from the point of view of the macromolecular bonds, which depends on the mutual orientation of the macromolecules under the influence of thermal movement and flow. This also embraces the cause of the thixotropic changes, hysteresis phenomena and nature of the variation of $\tau_f/\tau_{stat.}$ with changes in c, D and t°.

After the general characteristics of the rheological properties let us now turn to the question of the invariant function $D(\tau)$ for ethylcellulose solutions and the applicability of Weissenberg's method [7] to the case. Figure 6 shows the results of comparison, for 8 per cent and 10 per cent solutions, of the curves for average rate of shear obtained in a capillary viscometer, $\log D=\varphi(\log \tau_R)$ (curve 1′ corresponds to the 8 per cent and curve 1 to the 10 per cent solution), and the characteristic flow curves $\log D_R=f(\log \tau_R)$, obtained in the rotational viscometer (curve 2′ corresponds to the 8 per cent and curve 2 to the 10 per cent solution). Here $\tau_R=\Delta PR/2L$ is the shear stress at the wall of a capillary of radius R and length L, ΔP is the pressure drop in the capillary; $D=Q/\pi R^3$ is the average rate gradient across a section of the capillary, where Q is the delivery from the capillary per sec.

It follows from Fig. 6 that the results with the capillary viscometer (curves 1′ and 1) calculated according to the equation $D_R=D(3+(d \log D/d \log \tau_R))$ [2] correspond with the right hand branches of curves 2′ and 2 obtained with the rotational viscometer. The satisfactory agreement between the results with the rotational viscometer, calculated according to Weissenberg, and from measurements in the capillary viscometer indicate conclusively the invariance of the function $D(\tau)$ determined by different methods. The calculated points lie on the right and not the left branches of the characteristic flow curves. The right hand branches of the curves correspond to tests at the lowest degree of breakdown of the system. In measurements with a capillary viscometer fresh portions of solvent, not having been subjected to high rate gradients, are continuously entering the capillary. It is for this reason that the results with the capillary viscometer correspond with the right hand branches of the flow curves obtained with the rotational viscometer. Similar results have been reported for pseudogels with a hydrocarbon solid phase [9]. It is quite

evident that just as it is possible to pass from flow curves obtained from capillary-viscometry data to characteristic curves it is possible to proceed from characteristic curves to flow curves at average rate of shear.

The invariance of the function $D(\tau)$ enables recommendations to be made about the possibility of pumping these systems through cylindrical pipes under conditions of laminar flow. Actually the right hand branches of the characteristic

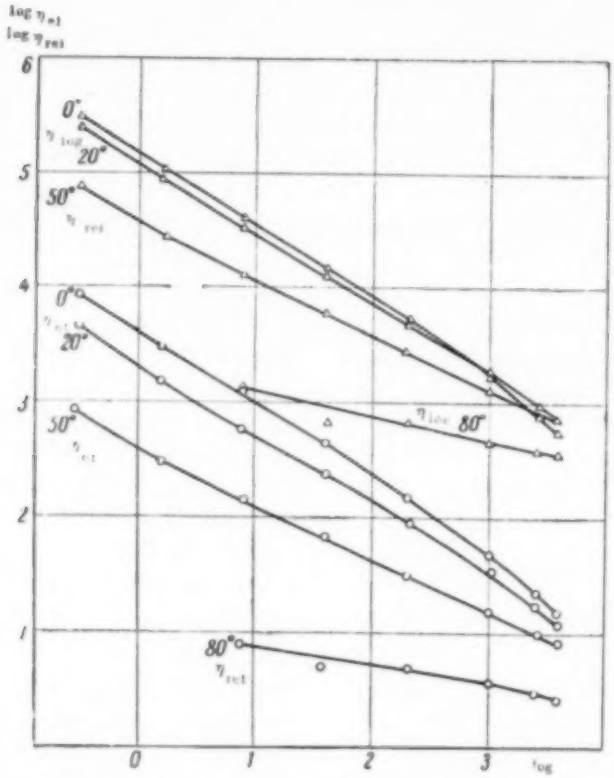

FIG. 5. Dependence of the effective and relative effective viscosity of a 15% solution of ethylcellulose on rate of deformation at various temperatures.

curves (Fig. 3a and 4) can be considered, with sufficient accuracy for practical purposes; to be two straight lines, each of which is determined by a power function of the type $D=m\tau^n$, where m and n are constants, easily found graphically. Taking this relationship into account the delivery per second through a cylindrical tube of radius R and length L will be $Q=[\pi m/(n+3)]\,(\Delta P/2L)\,R^{n+3}$, where ΔP is the difference in pressure between the ends of the tube. The average rate of movement of solution in the tube is $V_{av.}=[m/(n+3)]\,(\Delta P/2L)^n R^{n+1}$. The relationship between the mean rate gradient (D) and the rate gradient at the

tube wall (D_R) will be $D=D_R/(n+3)$. Consequently, having obtained by a suitable method the characteristic flow curves of solutions of ethylcellulose or

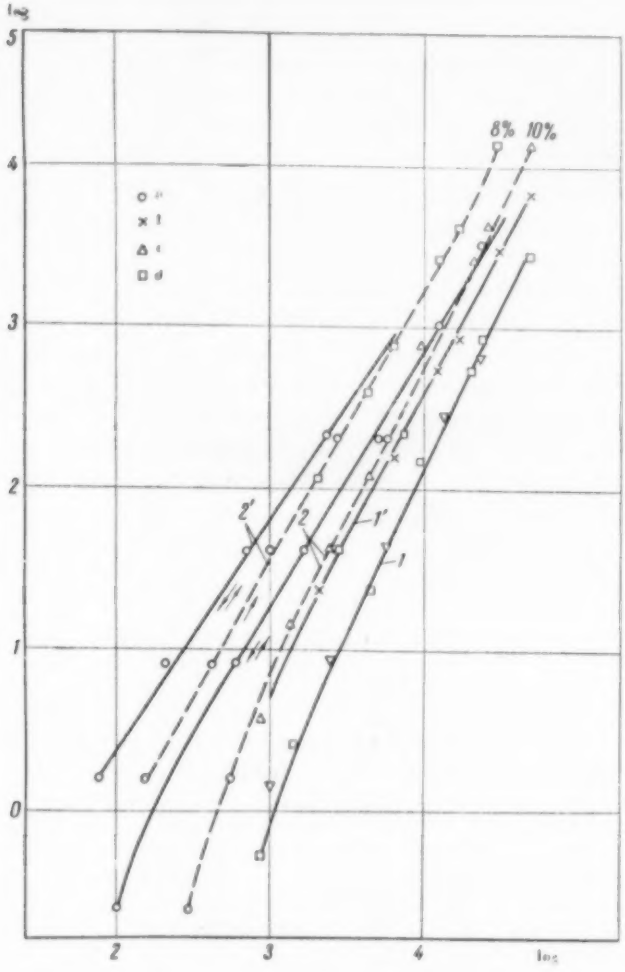

FIG. 6. Flow curves of ethylcellulose solutions: (a) and (b) directly for experimental data; (c) calculated from capillary-viscometer results; (d) calculated from rotational-viscometer results.

similar systems, it is possible to calculate by means of the above equations, their movement through tubes, taking account of hysteresis phenomena and thixotropic changes without fail.

CONCLUSIONS

In connection with the practical value of solutions of cellulose esters, with the possibility of using them in photo-elasticity and photo-viscosity methods for modelling various deformation processes, and with the interest in systems intermediate between pastes (pseudogels) and elastic, non-Newtonian liquids, the general rheological characteristics of concentrated solutions of ethylcellulose in methylcellosolve, which is a relatively poor solvent for this polymer, are given. The gel strength and viscosity properties of solutions containing from 5 and 20 g of ethylcellulose per 100 ml of methylcellosolve, from −20 to 80°, have been investigated. The viscosity properties were studied over a range of change in deformation rate of four orders. The systems studied are characterized by considerable thixotropy and they differ from typical pastes (pseudogels) in their higher elasticity, greater dependence of yield value on rate of deformation and a marked decrease in relative effective viscosity with increasing temperature. As in the case of pseudogels the ratio of the yield value to the shear stress at steady flow can decrease with increasing rate of deformation. This ratio does not vary monotonically with temperature and concentration.

A comparison has been made of viscosity measurements in rotational and capillary viscometers and it is shown that the capillary viscometry data correspond to tests in the rotational viscometer of solutions that have not been subjected to high rates of deformation.

Translated by E. O. PHILLIPS

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THE LOW TEMPERATURE COPOLYMERIZATION OF ISOBUTYLENE WITH SMALL AMOUNTS OF DIENE HYDROCARBONS IN THE PRESENCE OF BORON TRIFLUORIDE*

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A COMPARATIVELY small number of papers [1–6] and a very large number of patents are devoted to the study of the low temperature copolymerization of isobutylene with small proportions of diene hydrocarbons. The question of the effect of the nature and concentration of the diene hydrocarbons on the copolymerization reaction with isobutylene has not been sufficiently examined, though this factor is of great importance from both the theoretical and practical points of view. The present paper gives the results of an investigation of the low temperature copolymerization of isobutylene with diene hydrocarbons in polar and non-polar solvents in the presence of boron trifluoride. On the basis of these results some views are expressed on the nature of the reaction.

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EXPERIMENTAL

Starting materials and method of copolymerization.

(1) Isobutylene, concentration 97·5–98% by volume, after removal of alcohol, aldehyde and water.

(2) Ethyl chloride, purified by sulphuric acid, washed with water and dried succesively with calcium chloride and activitated alumina, contained 0·0002% moisture and 0·001% ethyl alcohol.

(3) Liquid ethylene, concentration 99·8–100% by volume.

(4) Boron trifluoride, contained as impurities: SO_2 0·03%, So_3 0·1% and SiF_4 0·2%.

(5) Butadiene, obtained from butadiene tetrabromide [7], concentration 98·5–99%.

(6) Isoprene, separated from the technical material by rectification, distilled over the range 33·8–34°; d_4^{20} 0·6803, n_D^{20} 1·4216.

(7) 2,3-Dimethylbutadiene-1,3, obtained by dehydration of pinacone with acetic anhydrine [8]. After purification it distilled over the range 69–69·5°; d_4^{20} 0·7264, n_D^{20} 1·4374.

* Vysokomol. soedin. **2**: No. 3, 354–359, 1960.

(8) Chloroprene, redistilled over the range 59·0–59·5°; d_4^{20} 0·9548, n_D^{20} 1·4580.
(9) Fluoroprene, b.p. 11·5–12·0°C.

The copolymerization experiments were carried out by the method described in a previous communication [9]. The isobutylene solution, the co-catalyst (isobutyl alcohol) and diene hydrocarbon in liquid ethylene or in an ethylene-ethyl chloride mixture, and a solution of boron trifluoride in ethylene were run in simultaneously to a glass vessel immersed in a Dewar flask containing ethylene. After mixing the solutions the total monomer concentration was 1·0 mole/l., boron trifluoride 0.03 mole/l. and co-catalyst * 0.004 mole/l. Sixty seconds after commencement of copolymerization the reaction was stopped by the addition of 50 ml of a 1% solution of *p*-tert-butylphenylsulphide in ethyl alcohol. The copolymer formed was freed from solvent and other additives by heating to constant weight at 105°/10 mm.

The viscosity average molecular weight was determined by a single measurement [10] and calculated according to the equation [11]:

$$\log M = 5{\cdot}378 + 1{\cdot}56 \log [\eta].$$

Analysis of the copolymers for unsaturation [12] was carried out on reprecipitated samples.

RESULTS

The rate of polymerization of isobutylene in ethylene solution falls rapidly with small additions of diolefines (0·01–0·05 mole/l.), particularly in the case of isoprene. At concentrations below 0·01 mole/litre the retarding effect of diolefines could not be detected because after 60 seconds more than 80% of the isobutylene had reacted.

Polymers of molecular weight $5{\cdot}0–5{\cdot}5 \times 10^6$ are formed in the polymerization of pure isobutylene. The addition of very small quantities of diene hydrocarbons (0·001–0·0025 mole/l.) leads to the formation of copolymers of considerably lower molecular weight. The nature of the diolefine has a considerable effect on the change in molecular weight of the copolymers. This effect is particularly marked in the case of isoprene. For example, increasing the concentration of isoprene in the initial reaction mixture to 0·01 mole/l. results in a fall in molecular weight to $0{\cdot}25 \times 10^6$. Polymers of isobutylene with butadiene and 2,3-dimethylbutadiene-1,3 at the same concentration of these in the initial mixture have higher molecular weights (about $1{\cdot}0 \times 10^6$) (Fig. 2a).

The copolymers of isobutylene with isoprene and 2,3-dimethylbutadiene-1,3 obtained from mixtures in which the concentration of these additives is low (0·0025–0·025 mole/l.) have almost the same degree of unsaturation, which is approximately equivalent to half the concentration of diolefine added. When higher concentration of diolefines in the initial mixture are used the unsaturation of the copolymers is less than half of that equivalent to the added diolefine.

* No co-catalyst was used in copolymerizations in ethylene-ethyl chloride solution.

On polymerization of isobutylene mixed with butadiene, at low initial concentrations of the latter (up to 0·01 per cent the polymers show no unsaturation and copolymers with low degrees of unsaturation are formed only at higher concentrations (Fig. 2b).

On copolymerization of isobutylene with diolefines in a mixture of ethyl chloride and liquid ethylene (1:1) at an initial temperature of −103° the same relationships are found as for polymerization in pure ethylene. However the increase in polarity of the medium, contributed by the ethyl chloride, leads to some increase in reaction rate. Low initial concentrations of the diolefines have a lower retarding effect on the polymerization rate (Fig. 1b). The addition of butadiene up to a concentration of 0·02 mole/l. has practically no effect on the reaction rate, probably as a result of homopolymerization because the polymers formed are not unsaturated. The molecular weights of the copolymers formed in the polar solvent are higher than those formed in the non polar solvent (Fig. 2b). The reverse effect is observed in the polymerization of pure isobutylene; in liquid ethylene polymers are formed of higher molecular weight than those in a mixture of ethylene and ethyl chloride [13].

In all probability only polyisobutylene is formed in the polymerization of isobutylene in the presence of fluoroprene.

Thus, an increase in the concentration of fluoroprene leads to a decrease in reaction rate and in the molecular weight of the products, at the same time the unsaturation of the polymers remains unchanged and lies within the limits of experimental error.

Polymerization of isobutylene in the presence of chloroprene (0·02–0·10 mole/l.) yields polymers containing brown inclusions of another polymer. With increasing initial concentration of chloroprene a decrease in reaction rate and in the molecular weight of the polymers is observed, but to a greater extent in the case of fluoroprene. As a specific example, at a chloroprene concentration of 0·10 mole/1.)

TABLE 1. COPOLYMERIZATION OF ISOBUTYLENE WITH FLUOROPRENE IN A MIXTURE OF ETHYLENE AND ETHYL CHLORIDE (1:1) IN THE PRESENCE OF 0·03 MOLE/l. OF BORON TRIFLUORIDE FOR A PERIOD OF 1 MIN

Concentration of isobutylene (mole/l.)	Concentration of fluoroprene (mole/l.)	Conversion %	$[\eta]$	$\bar{M} \times 10^{-6}$	Unsaturation (mole %)
1·00	0·00	93·5	4·98	2·92	0·05
0·98	0·02	74·8	2·69	1·12	0·15
0·97	0·03	70·7	2·07	0·72	0·15
0·96	0·04	68·4	1·38	0·39	0·18
0·94	0·06	66·0	1·17	0·30	0·18
0·92	0·08	57·5	1·03	0·25	0·19
0·90	0·10	56·2	1·06	0·26	0·18

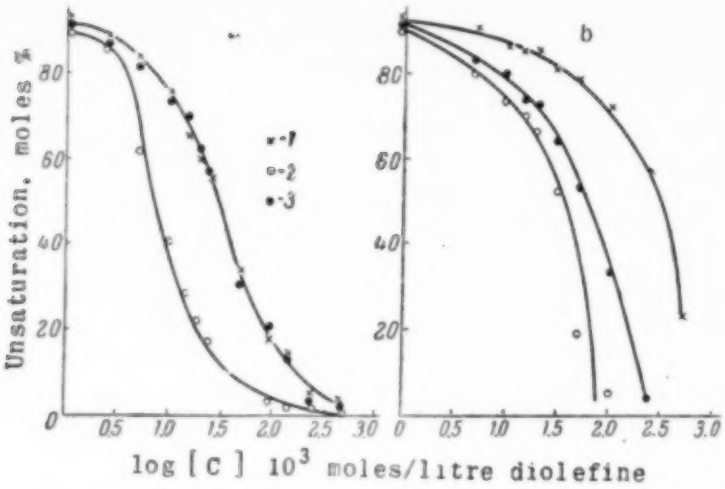


Fig. 1. Dependence of the degree of copolymerization of isobutylene with diene hydrocarbons on the nature and concentration of the diolefine: 1—in solution in ethylene; b—in a mixture of ethylene and ethyl chloride. (1) butadiene, (2) isoprene, (3) 2,3-dimethylbutadiene-1,3.

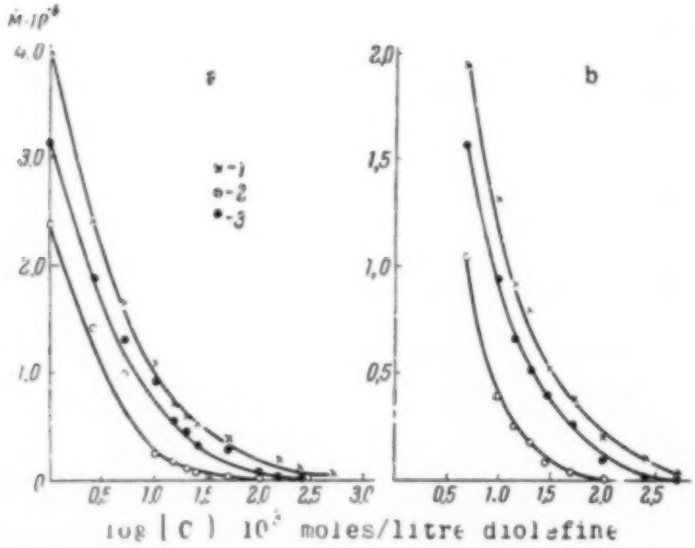


Fig. 2. Dependence of the average molecular weight of the copolymers on the nature and concentration of the diene hydrocarbons: a—in solution in ethylene; b—in a mixture of ethylene and ethyl chloride. (1) butadiene, (2) isoprene, (3) 2,3-dimethylbutadiene-1,3.

the degree of conversion after 1 minute was 32–35 per cent and the molecular weight of the polymer was within the range $0{\cdot}15–0{\cdot}17 \times 10^6$. The bulk of the polymer was saturated. The composition of the inclusions was not investigated.

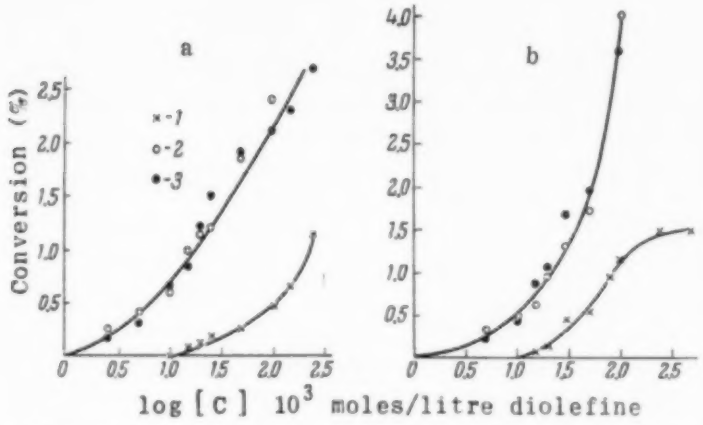
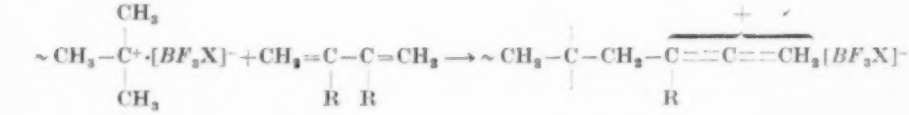


FIG. 3. Dependence of the unsaturation of the copolymer on the nature and concentration of the diene hydrocarbons: 1 – in solution in ethylene; b – in a mixture of ethylene and ethyl chloride. (1) butadiene, (2) isoprene, (3) 2,3-dimethylbutadiene-1,3.

DISCUSSION

The basic cause of the negative action of diene hydrocarbons in copolymerization with isobutylene in the presence of boron trifluoride is that the complexes formed at the ends of the polymer chains, containing diene-hydrocarbon units, are of low reactivity and hence are able to terminate the chain. The decrease in activity of the complexes is brought about by the fact that the positive charge at the end of the polymer chain is weakened by its distribution over at least three carbon atoms, and in the case of halogenated diene hydrocarbons, over the halogen atom also.



where R is alkyl, H or halogen.

The charge on the terminal carbon atom will be insufficient for the addition of a molecule of isobutylene.

Obviously the activity of the terminal complex with respect to the addition of isobutylene will vary in relation to the nature of the diene hydrocarbon in the following order:

$$CH_2=\underset{Cl}{C}-CH=CH_2 < CH_2=\underset{F}{C}-CH=CH_2 < CH_2=CH-CH=CH_2 <$$

$$< CH_2=\underset{CH_3}{C}-CH=CH_2 < CH_2=\underset{CH_3}{\overset{CH_3}{C}}-C=CH_2.$$

Furthermore the addition of the diene hydrocarbons to growing polyme. chains containing terminal isobutylene units will also proceed at different ratesr depending on their structure, in the descending order

$$CH_2=\underset{CH_3}{\overset{CH_3}{C}}-C=CH_2 > CH_2=\underset{CH_3}{C}-CH=CH_2 > CH_2=CH-CH=CH_2 >$$

$$> CH_2=\underset{F}{C}-CH=CH_2 > CH_2=\underset{Cl}{C}-CH=CH_2.$$

It is quite obvious that an increase in concentration of diene hydrocarbon in the reaction mixture will lead to a decrease in reaction rate and an increase in the rate of chain termination, consequently the molecular weight of the copolymers will fall.

Another cause of the retarding action of diene hydrocarbons in copolymerization with isobutylene is that they probably react more readily than isobutylene or the co-catalyst with boron trifluoride with the formation of stable complexes, of low activity at low temperatures, that are not capable of initiating polymerization.

Thus the diene hydrocarbon in the initial stage of initiation combines with part of the boron trifluoride so that its concentration in the reaction system is considerably reduced and consequently the rate of polymerization is also reduced. The negative action of diene hydrocarbons is weakened to some extent by carrying out the copolymerization in a polar solvent and consequently the reaction rate and molecular weight of the copolymer increase a little.

CONCLUSIONS

(1) The low temperature copolymerization of isobutylene with diene hydrocarbons in the presence of boron trifluoride has been studied in polar and non-polar solvents.

(2) It is shown that in the copolymerization of isobutylene with diene hydrocarbons the nature and concentration of the latter has a substantial effect on the reaction rate and on the molecular weight and unsaturation of the copolymers. (a) On copolymerization of isobutylene with fluoro- and chloroprene separate homopolymerization occurs. (b) Of a series of diene hydrocarbons the most active for copolymerization with isobutylene is 2,3-dimethylbutadiene-1,3 and the least

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active is butadiene. The latter does not form copolymers when present at low concentrations in the reaction mixture. (c) Diene hydrocarbons act as reaction poisons in copolymerization with isobutylene because in their presence, even at low concentrations, there is some decrease in rate and a sharp fall in molecular weight.

Translated by E. O. PHILLIPS

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CATALYTIC COPOLYMERIZATION OF STYRENE AND BUTADIENE*

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STYRENE-BUTADIENE copolymers obtained by emulsion polymerization with peroxide-type initiators form the basis of present-day, mass-produced synthetic rubbers. Naturally the mechanism of the radical chain polymerization of mixtures of styrene and butadiene has repeatedly been the subject of investigation. The catalytic copolymerization of this system has not been studied in detail. It is known that in the copolymerization of styrene and butadiene by metallic sodium [1, 2] and by "Alfin catalysts" [3], in contrast to radical polymerization, styrene is the more active monomer because the polymer formed in the early stages of polymerization is rich in styrene units. Our preliminary experiments showed that on polymerization of mixtures of these monomers by butyllithium a copolymer of low styrene-unit content is formed, i.e. styrene is the less active monomer. This inconsistency was the reason for the present investigation, begun with a study of the kinetics of the separate polymerization of styrene and butadiene by butyllithium in benzene, i.e. under homopolymerization conditions.†

On the example of the polymerization of isoprene [5] it has been shown that the kinetics of catalytic homopolymerization can be satisfactorily described if the existence of three component reactions is assumed:

(1) initiation:

$$N + M \xrightarrow{k_1} M_1N;$$

(2) propagation

$$M_iN^* + M \xrightarrow{k_2} M_{i+1}N^*;$$

(3) termination

$$M_iN^* + M_jN^* \text{ (or } N) \xrightarrow{k_3} NM_i + NM_j \text{ (or } N)$$

* Vysokomol. soedin. **2**: No. 3, 365–376, 1960.

† The basic results of the investigation were reported at the 11th Conference on Macromolecular Compounds [4].

where M and N are the monomer and catalyst, $M_i N^*$ and $M_j N^*$ are active, growing polymer molecules and NM_i and NM_j are organometallic macromolecular compounds.

The greatest difference between catalytic homopolymerization by butyllithium and radical, chain polymerization lies in the nature of the termination reaction. In radical polymerization each act of termination involves the disappearance of two active polymerization centres, i.e. of two free radicals. In catalytic polymerization, on chain termination by the interaction of two active molecules each elementary act leads to the formation of two organometallic molecules (NM_i and NM_j), possessing the properties of the original catalyst, i.e. capable of again starting active polymerization centres on interaction with a monomer molecule.

The kinetic equation of the over-all polymerization reaction, consisting of the three component reactions mentioned, is rather complex in form

$$x = \frac{m_0 - m}{m_0} = \frac{k_2 n_0}{k_1 m_0} - \frac{1}{\left(1 + \frac{k_3 n_0}{k_1 m_0}\right)^2} \cdot \left\{ \left(1 + \frac{k_3 n_0}{k_1 m_0}\right) k_1 \varphi - 1 + \exp\left[- \left(1 + \frac{k_3 n_0}{k_1 m_0}\right) k_1 \varphi \right] \right\},$$

where k_1, k_2 and k_3 are the rate constants of the component reactions, m_0 and m the initial concentration of monomer and the concentration at time τ, $n_0 = \sum_{i=0}^{\infty} [M_i N] + \sum [M_i N^*]$ the initial catalyst concentration, x the degree of conversion and φ the conventional time, which is determined by the equation $\varphi = \int_0^{\tau} m d\tau$ and can be derived graphically with sufficient accuracy from the experimental data [6].

If it is assumed that in the polymerization of butadiene and styrene, even in a good solvent such as benzene, $k_3 \ll k_1$ the above kinetic equation becomes considerably simplified. Since in our experiments $n_0 \ll 1 < m_0$, then $k_3 \cdot n_0 / k_1 \cdot m_0 \ll 1$, and hence can be neglected when the equation takes the form

$$x = \frac{k_2 n_0}{k_1 m_0} (k_1 \varphi + e^{-k_1 \varphi} - 1)$$

Even at relatively low degrees of conversion the following inequality holds

$$e^{-k_1 \varphi} \ll 1 < k_1 \varphi$$

and the kinetic equation becomes linear

$$x = \frac{k_2 n_0}{k_1 m_0} \cdot (k_1 \varphi - 1)$$

In an experimental study of the reaction kinetics n_0 and m_0 are always known and the derived values x_i and φ_i can be chosen such that the linearity of the

equation is maintained. Hence there is no difficulty in determining the two constants k_1 and k_2 with an accuracy of not less than 10% (relative) by the analytical or graphical method.

If $k_2/k_1 > 1$ and the ratio $n_0/m_0 \ll 1$ and is kept constant in all the experiments (in our work $n_0/m_0 \cong 0{\cdot}01$), then with a small difference (a few kcal/mol) in the activation energies of the initiation and termination reactions it may be taken than the expression $1+(k_2 \cdot n_0)/k_1 \cdot m_0) = c \cong \text{const.}$ and is independent of temperature over a narrow range. Then the kinetic equation takes the form

$$x = \frac{k_2}{c} \cdot \frac{1}{ck_1} \cdot \frac{n_0}{m_0} \left\{ ck_1\varphi - 1 + e^{-ck_1\varphi} \right\}.$$

Consequently in this case it is possible to calculate from the experimental data only the values of k_2/c and $c \cdot k_1$. Since the values of the apparent energy of activation of the two component reactions can be found fairly accurately,

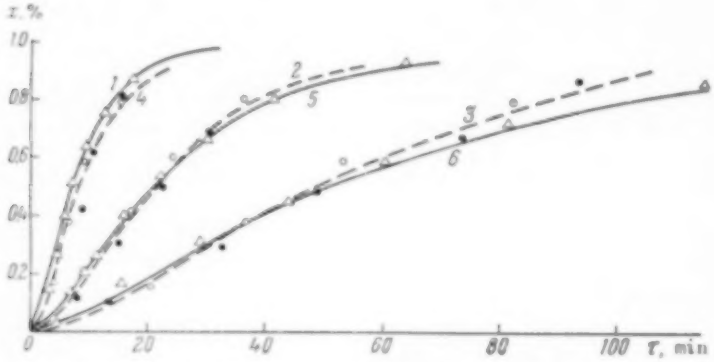

FIG. 1. Kinetic curves of the homopolymerization of styrene (curves 2, 3 and 4) and of butadiene (curves 1, 5 and 6). (1) 50°; (2) 20°; (3) 10°; (4) 30°; (5) 40°; (6) 30°. The reaction rate constants given in Table 1 were used for plotting the curves.

the values of the pre-exponential factors will differ from the true values by a factor of $1/c$ in the first case and of c in the second case. It is taken in what follows that $k_2 < k_1$.

It was found that in homopolymerization by butyllithium styrene is a considerably more active monomer than butadiene. The kinetic curves at 10, 20 and 30° for the first practically coincide with those for the second at 30, 40 and 50° respectively (Fig. 1).

Judging by the values of the constants of the component reactions, calculated by the above method, this difference in activity is brought about by the higher activity of styrene in both the initiation and propagation reactions (see Table 1 and Fig. 2).

The following are the essential facts. In the polymerization of styrene, as would be expected, the apparent activation energy of initiation is rather higher (by about 2000 cals) than that of propagation at values of the pre-exponential factor that are the same within the limits of experimental error. In the polymerization of butadiene there is a rather unusual relationship: a very high (18·0 kcal/mole) activation energy of propagation was found, with a relatively low

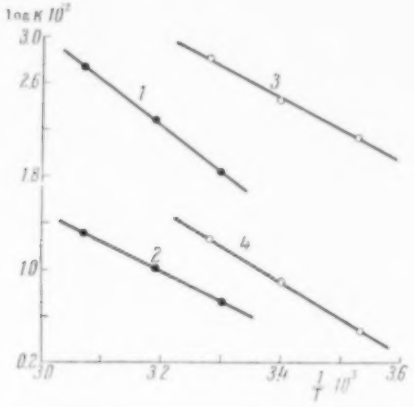

FIG. 2. Dependence of log k on the inverse of the absolute temperature, for butadiene, (1) for k_2, (2) for k_1: and for styrene, (3) for k_2 and (4) for k_1.

(11·5 kcal/mole) activation energy of initiation. The considerable over-all reaction rate is connected with an exceptionally high value of the pre-exponential factor, or in other words, with the exceptionally favourable steric factor of the formation of a transition state. This latter circumstance leads to a very interesting phenomenon in the copolymerization of styrene and butadiene by butyllithium. Independently of temperature and monomer concentration (see Fig. 3, a, b and c) and also of catalyst concentration, in the first place butadiene polymerizes with a small quantity of styrene at a rate specific to the homopolymerization of butadiene. When the main part of the butadiene has been used up and its concentration in the remaining monomer reaches 5–8 per cent styrene begins to polymerize, with small amounts of butadiene, at the rate specific to pure styrene. Probably in the polymerization of butadiene by butyllithium the active polymerization centres, consisting of complexes of an ion-dipole character, exert a long range effect. It may be thought that this effect consists in the polarization of the butadiene molecules present in the field of an active centre and the formation around the latter of a sheath of orientated monomer molecules. Hence although the repulsive force between the reacting molecules is relatively great (apparent activation energy 18 kcal/mole), because of the high degree of orientation of the monomer molecules the propagation rate is fairly high. In the inter-

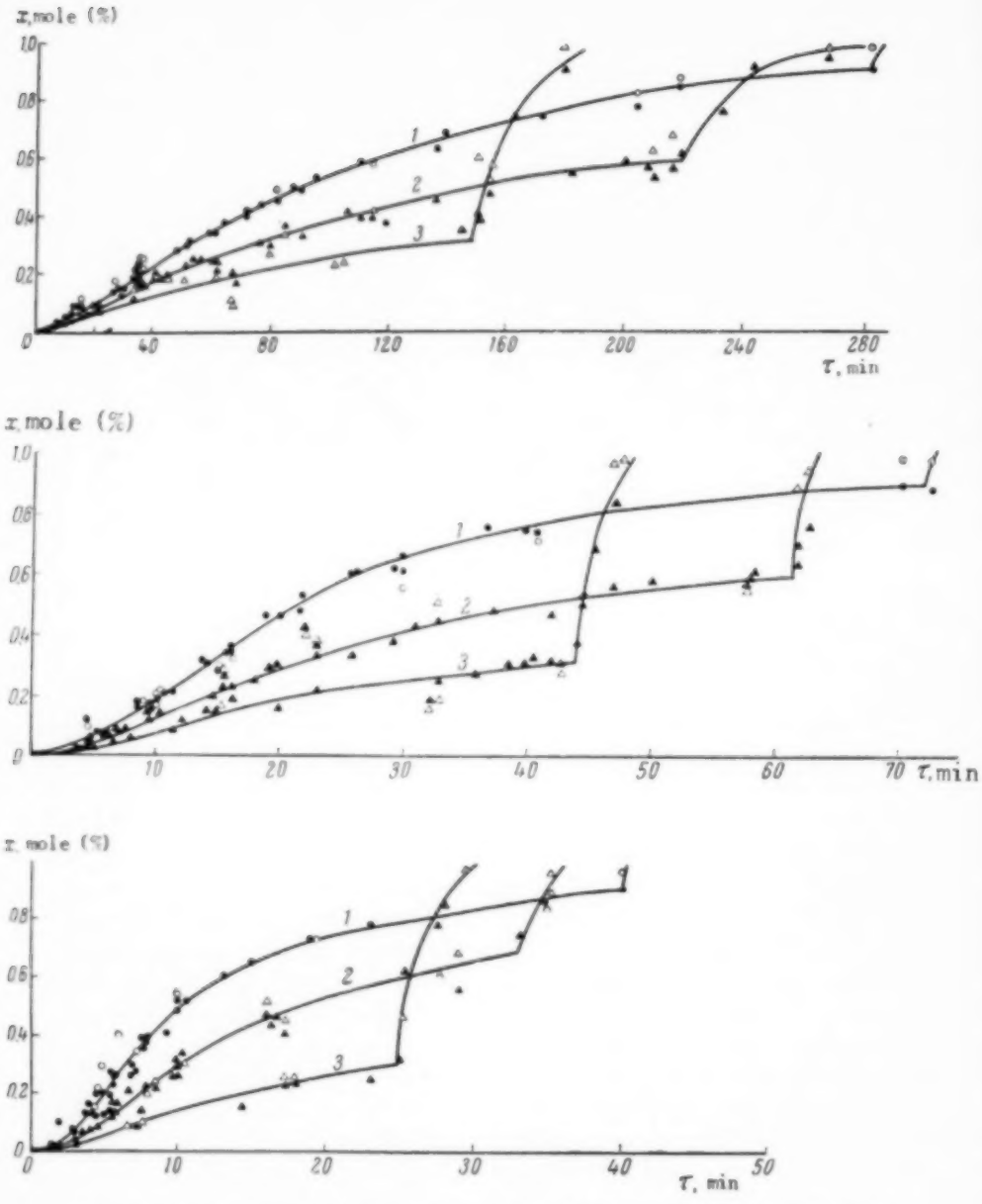

FIG. 3. Kinetic curves of the copolymerization of styrene and butadiene. Styrene/ /butadiene ratios: 1:4 (1); 1:1 (2) and 1:0·33 (3). ▲● – from the volume contraction of the reaction mixture; △○ – from the weight of polymer formed; (a) at 30°; (b) at 40°; (c) at 50°C.

action of butadiene with organolithium compounds (the orginal butyllithium or new, macromolecular organolithium compounds formed during polymerization) a similar "solvation" is absent, which leads to a lowering of the apparent activation energy and to a certain extent of the frequency of collision of orientated reacting molecules (the frequency factor is six orders lower than that for propagation).

TABLE 1. VALUES OF THE RATE CONSTANTS OF THE COMPONENT REACTIONS, THE APPARENT ACTIVATION ENERGIES AND PRE-EXPONENTIAL FACTORS IN THE POLYMERIZATION OF STYRENE AND BUTADIENE IN BENZENE.

Monomers	Styrene			Butadiene		
Reaction temperature °C	10·3	20·7	31·9	30·4	40·9	82·9
Initial concentration (moles/l.):						
Monomer	1·77*	1·75*	1·72*	2·36	2·26	2·57
Butyllithium	0·015	0·019	0·019	0·024	0·023	0·026
Values of constants (g-moles/l./min):						
k_1	0·03	0·08	0·18	0·05	0·10	0·20
k_2	1·4	2·8	6·5	0·7	1·9	5·3
Values of the pre-exponential factor and activation energy (kcal):						
Initiation reaction	$1·07 \times 10^{10}$; 14·0			$1·05 \times 10^{7}$; 11·4		
Propagation reaction	$0·8 \times 10^{10}$; 12·3			$0·7 \times 10^{13}$; 18·0		

* Mean of two experiments.

In the polymerization of styrene there is also no such "solvation" sheath. The polarizing action of both the organolithium compounds and the active centres reaches only near monomer molecules and hence in both cases the frequency factor is of the same order (10^{10}). However the forces of repulsion in the transition state are considerably less in the propagation reaction, i.e. in the reaction between monomer molecules and active centres. (The apparent activation energy is 12 kcal/mole as compared with 14 kcal/mole in the reaction with organolithium compounds).

In copolymerization of butadiene and styrene the active centres, being "screened by a solvated sheath" of the former, are not very accessible to styrene molecules, consequently the semblance of a greater activity of butadiene arises.

If we proceed from the normally accepted hypothesis that the composition of a copolymer is determined only by the values of the copolymerization constants α and β, i.e. by the ratio of the constants of the propagation reaction, then it is easy to derive these values graphically using the fully integrated copolymeriza-

tion equation [7]*. From the experimental copolymer compositions at 10 and 20 per cent conversion and at three ratios of styrene to butadiene, namely

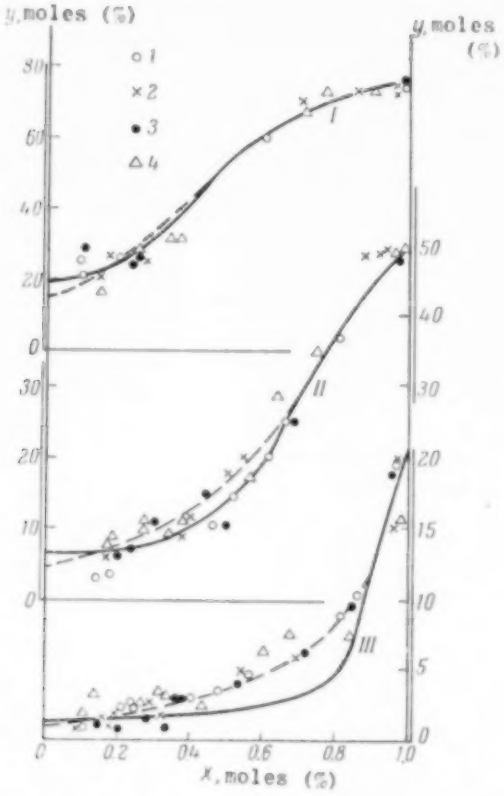

FIG. 4. Dependence of content of styrene units in the copolymer (y) on the degree of conversion (x). Styrene/butadiene ratios: (I) 1:0·33; (II) 1:1 and (III) 1:4. Experimental points: concentration of butyllithium 0·02 mole/litre at 30°—1; 40°—2 and 50°—3; concentration of butyllithium 0·0033 mole/litre at 50°—4. Continuous curves calculated for $\alpha = 0{\cdot}05$ and $\beta = 15$, dotted curves for $\alpha_1 = 0{\cdot}05$, $\beta_1 = 20$ and $\gamma_1 K = 4$.

* For the graphical derivation of the copolymerization constants and for the construction of the graph of copolymer composition against degree of conversion it is convenient to use the integrated copolymerization equation in the following form.

$$\log \frac{B_0 - (x - xy)}{B_0} - \beta \log \frac{A_0 - xy}{A_0} = \left(\frac{1}{P} + \beta\right) \left\{ \log \left(\frac{A_0}{B_0} - \frac{1}{P} \right) - \log \left[\frac{A_0 \cdot xy}{B_0 \cdot (x - xy)} - \frac{1}{P} \right] \right\},$$

where $P = (1 - \alpha)/(1 - \beta)$, α and β are the copolymerization constants, A_0 and B_0 the relative initial concentrations of the monomers ($A_0 + B_0 = 1$), x the degree of conversion expressed as a fraction and y the content of units of the first monomer (A) in the copolymer, also expressed as a fraction.

0·77:0·23, 0·5:0·5 and 0·2:0·8, the values found for the copolymerization constants for the styrene-butadiene system were $\alpha = 0{\cdot}05$ and $\beta = 15$.

The graph of copolymer composition against degree of conversion (Fig. 4) shows that only at high styrene concentrations in the initial mixture do the experimental points fit the curve constructed on the basis of the integrated copolymerization equation, using the values of α and β quoted above, within the limits of experimental error resulting from inaccuracy in measuring out the monomers and errors in the determination of the styrene-unit content of the copolymer (continuous curve I). At equal initial concentrations of styrene and butadiene most of the experimental points lie above this curve (curve II) and at a low styrene content they lie off the curve over the greater part of its length (Fig. 4, curve III). By increasing the value of α or decreasing β it is possible to find by the method of trial and error values such that curve III fits the experimental points at a conversion of 0·6 to 0·8 but then curves I, II and III will lie considerably above the points in the region of low conversion ($x \cong 0{\cdot}2$). The calculated curves can follow closely the experimental points through their whole course at all three styrene concentrations if the values of α and β are related to the fractional concentration of butadiene: α must be increased and β decreased with increasing conversion and butadiene concentration. Such a relationship is possible if the butadiene copolymer formed has a substantial effect on the course of the copolymerization reaction. It is known [8] that symmetrically substituted ethylene hydrocarbons are capable of forming so-called π-complex compounds with electron-acceptor compounds. For example, pseudo butylene, like ethers, accelerates the polymerization of butadiene by butyllithium [8]. In the polymerization of butadiene by butyllithium most of the monomer molecules combine in the 1,4-position, i. e. the polymer molecules contain units having the structure of symmetrically substituted ethylene hydrocarbons $\cdots CH_2\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH_2\cdots$, hence it may be considered that these take part in the formation of active centres of polymerization:

$$\cdots M\cdot RLi + \cdots CH{=}CH\cdots \rightleftarrows \cdots M\cdot RLi{:}\begin{matrix} CH\cdots \\ CH\cdots \end{matrix}$$

Consequently in the copolymerization of butadiene and styrene there will be two types of active centre: (a) "simple", formed from active end groups of the polymer molecules ($\cdots M\cdot BLi$) and (b) "complex", containing additional groups from the middle sections of the polymer molecules ($\cdots M\cdot RLi{:}(CH)_2\cdots$). Each type of active centre must have its own, characteristic value for the copolymerization constants which may be denoted as α_1 and β_1 for the first type and α_2 and β_2 for the second. The resultant values of the apparent copolymerization constants will be given by the equations

$$\alpha = \alpha_1 c + \alpha_2 (1-c) \text{ and } \beta = \beta_1 c + \beta_2 (1-c)$$

where c is the fractional concentration of the first type of active centre.

On the other hand the concentration of the second type is connected with the equilibrium constant for the above reaction according to the equation

$$K = \frac{(1-c)}{c([B_0]-[B])}$$

where $[B_0]$ and $[B]$ are the concentration of butadiene initially and at the time in question.

Let us put $\alpha_2 = \gamma_1\alpha_1$ and $\beta_2 = \gamma_2\beta_1$, then the solution of the system of equations obtained will be as follows

$$\alpha = \frac{1+\gamma_1 K([B_0]-[B])}{1+K([B_0]-[B])}\alpha_1 \text{ and } \beta = \frac{1+\gamma_2 K([B_0]-[B])}{1+K([B_0]-[B])}\beta_1.$$

$([B_0]-[B])$ is always less than 1 and the equilibrium of the reaction of formation of "complex" active centres tends toward the left, i. e. $K<1$ also; hence $K([B_0]-[B]) \ll 1$. Consequently it may be taken that the values of the apparent copolymerization constants are given with sufficient accuracy by the equations $\alpha = \alpha_1\{1+\gamma_1 K([B_0]-[B])\}$ and $\beta = \beta_1\{1+\gamma_2 K([B_0]-[B])\}$.

Naturally at zero conversion, i. e. when $[B]=[B_0]$, $\alpha=\alpha_1$ and $\beta=\beta_1$. The results obtained can be made use of for the calculation of α and β in the case where $\alpha_1\beta_1=1$ because after substituting the value of α the easily integrated differential equation

$$\frac{d[A]}{d[B]} = \alpha_1\{1+\gamma_1 K([B_0]-[B])\}\cdot\frac{[A]}{[B]},$$

is obtained, and after integration

$$\log\frac{[A]}{[A_0]} = \alpha\left\{(1+\gamma_1 K[B_0])\log\frac{[B]}{[B_0]} + \frac{[B_0]-[B]}{2{,}303}\gamma_1 K\right\}.$$

By introducing the symbols: x, the fractional degree of conversion and y the fractional content of units of the first monomer (styrene) in the copolymer, we obtain an expression more convenient for the construction of the calculated curves:

$$-\log[A_0]+\alpha_1\{1+\gamma_1 K[B_0]\}\log[B_0]+\log([A_0]-xy) =$$

$$= \alpha\{1+\gamma_1 K[B_0]\}\log([B_0]+xy-y)+\gamma_1 K\frac{x(1-y)}{2303}.$$

Since the product of the experimental, approximate values of α and β at a degree of conversion of 10–20 per cent was close to unity ($\alpha\beta = 0{\cdot}05\times 15 = 0{\cdot}75$) it was assumed that in our case $\alpha_1\,\beta_1=1$. It was found by the method of trial and error that with values of $\alpha_1=0{\cdot}05$ and $\gamma_1 K=4$ (correspondingly $\beta_1=20$ and $\gamma_2 K=0{\cdot}25$) the experimental points fall, within the limits of experimental error, about the theoretical curves, independently of the ratio of the monomer con-

centrations, of temperature (within the narrow limits of 30–50°), and of catalyst concentration (see Fig. 4, dotted curve). Thus for the copolymerization of styrene and butadiene by butyllithium in benzene solution it may be taken fairly reliably that $\alpha_1 = 0{\cdot}05$ and $\beta_1 = 20$.

The fact that the product of the constants is unity means that the relative activity of the active polymerization centres is independent of the terminal monomer unit. In other words both monomers give polymerization centres of approximately the same activity. This is essentially different from copolymerization by the free-radical, chain mechanism where the active monomer gives a polymerization centre, a free-radical, of low activity and conversely the monomer of low activity gives an active free radical.

In radical polymerization with a large difference in the activities of the copolymerizing monomers the phenomenon of a limiting degree of conversion is observed. With a relatively small amount of initiator the free radicals formed, by reacting with the highly active monomer form radicals of low activity which disappear almost completely by recombination or dispropotrionation. In the catalytic polymerization under discussion such reactions do not occur and therefore, naturally there is also no limiting degree of conversion.

After the more active monomer is used up the active centres remain, joined to the growing molecules and they continue to promote polymerization of the second monomer. As a result a block copolymer is obtained the molecules of which are in the form of a block consisting mainly of butadiene units, a small copolymer portion, and a block of styrene units. Direct determination of the content of polystyrene blocks by the oxidation method [9] showed that when there is a high styrene-unit content in the copolymer it occurs chiefly in blocks (Table 2).

TABLE 2. RESULTS OF EXPERIMENTS ON THE DETERMINATION OF THE CONTENT OF POLYSTYRENE BLOCKS IN THE POLYMER

Reaction temperature (°C)	Initial concentration (moles/l.)		Degree of conversion (%)	Content of styrene unit, (moles %)	
	Styrene	Butadiene		Total	In blocks
30	0·48	1·78	97·7	19	0
30	1·06	0·99	14·5	3	0
30	0·91	0·93	52·0	15	0
30	1·02	1·08	67·1	25	1·7
40	1·06	0·93	88·5	49	24
30	1·03	1·00	97·8	53	35
30	1·47	0·45	19·8	26	0
30	1·43	0·45	60·0	60	45
40	1·52	0·52	70·5	71	49
30	1·37	0·42	99·0	84	67
40	1·45	0·47	97·2	72	63

In the polymerization of pure butadiene in pseudo-butylene solution not only is an increase in polymerization rate observed but also an increase in the content of 1,2-butadiene units in the polymer. Hence a difference in concentration of "complex" active centres, connected in a complex way with the internal double bonds of the polymer, depending on the styrene concentration, should lead to a change in the 1,2-butadiene units in the polymer. Actually in the homopolymerization of butadiene in benzene the 1,2-unit content is 25 per cent (mean for three temperatures); in copolymerization, with initial styrene concentrations of 20, 50 and 70 per cent the contents of 1,2-butadiene units in the polymer (calculated on the total content of the latter) were 24, 20 and 18 per cent respectively. The fall in 1,2-butadiene-unit content on increasing the temperature from 30 to 50° was 3–5 per cent.

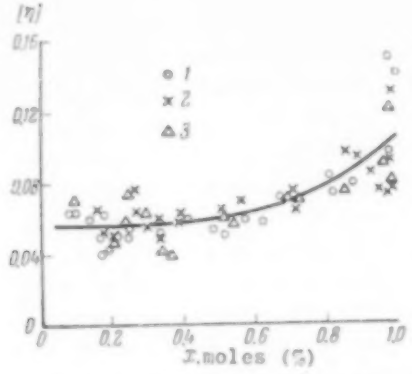

Fig. 5. Dependence of the intrinsic viscosity of the copolymers on the degree of conversion. Polymerization temperature: (1) 30°; (2) 40° and (3) 50°C.

The intrinsic viscosity of the polymers obtained up to a degree of conversion of 50–60 per cent was in the region of $0{\cdot}055 \pm 0{\cdot}010$ independently of reaction temperature and relative monomer concentrations. At higher conversions it increased a little. In the majority of experiments at a conversion of 95 per cent the intrinsic viscosity of the polymers was 0·075–0·100 and only in a few experiments was it 0·12–0·15, i. e. it agreed with the calculated value based on the assumption that each molecule of butyllithium forms one polymer molecule (see Fig. 5).

EXPERIMENTAL

Starting materials—Benzene was used as solvent because on polymerization in solution in saturated hydrocarbons the polystyrene and its copolymers formed at comparatively low degrees of conversion, precipitate from solution and disturb the homogeneity of the reaction. The benzene used had b. p. 80°, d_4^{20} 0·879 and n_D^{20} 1·5012. It was stored under nitrogen in the form of a benzene solution of butyllithium.

Butadiene was obtained by thermal decomposition of its complexes with monovalent copper salts. Analysis by reaction with maleic anhydride showed that the product contained 99·4% butadiene. The styrene, after laboratory redistillation, distilled at 60°/36 mm and had d_4^{20} 0·9060 and n_D^{20} 1·5458. Butyllithium in the form of a solution in benzene was prepared by the action of butyl chloride on metallic lithium. The butyllithium content of the solution was determined by the double titration method [10].

Method of polymerization—Polymerization was carried out in so-called double ampoules [5] consisting of two vessels (30–40 and 50–60 ml) connected by a tube graduated in 0·25 ml divisions and separated by a thin partition. Both parts of the ampoule were thoroughly dried *in vacuo* at 180–200° before filing. The solvent and monomers were placed in one vessel and the catalyst solution in the other. Entry of air was prevented during filling and sealing of the ampoules.

The reaction vessel was kept in a water thermostat for not less than 20 minutes before the start of an experiment, the partition was then broken by means of a glass rod placed in the ampoule and timing was begun. The course of polymerization was followed by means of the volume contraction of the contents of the vessel. When the desired degree of conversion was reached the vessel was immersed in a cooling mixture ($\sim -40°$), unsealed and about 5 ml of ethanol was added to the solution which was then thoroughly stirred. The contents of the ampoule were dissolved in benzene and the polymer was reprecipitated by methanol. After a second reprecipitation the polymer was dried *in vacuo*. The quantity of polymer formed was assessed both by weight and by the volume contraction of the reaction mixture. The volume contraction per mole of monomer polymerizing is approximately proportional to temperature and for butadiene and styrene is independent of the nature of the monomer (Fig. 6). This enables the degree of conversion to be assessed by means of the volume contraction of the reaction mixture in the copolymerization of butadiene and styrene. In all experiments the initial concentration of the monomers (total) was 2·1–2·3 moles/litre and of butyllithium about 0·02 mole/litre.

Analysis of the polymers—The content of styrene units in the polymer was estimated by means of the refractive index at 20°. For high styrene contents the determination was carried out at 50–60° and the correction for the change in refractive index with temperature was applied. The refractive index of polybutadiene was obtained by polymerizing butadiene with butyllithium at 30, 40 and 50°, in all cases it was found to be n_D^{20} 1·5155. The refractive index of polystyrene in the elastic state was taken as n_D^{20} 1·6014.

For some polymer samples the styrene-unit content was calculated from the results of elementary analysis, from the ratio of the carbon and hydrogen contents (%). At low proportions of styrene units in the polymer (up to 20 per cent) the results found from elementary analysis coincide with those from refractive index. In the region of high styrene content the former are somewhat lower than the latter but they lie within the limits of error of the measurements (Fig. 7).

The iodine number [11] of a large number of samples was determined. At high proportions of styrene units in the copolymer (above 20 per cent) the iodine

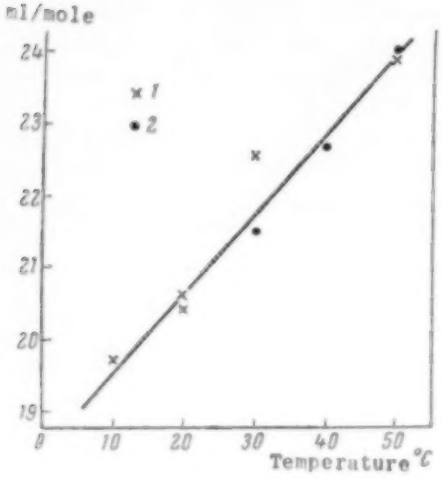

FIG. 6. Dependence of the specific volume contraction (ml/mole of monomer) of the reaction mixture on temperature in the polymerization of styrene (1) and butadiene (2).

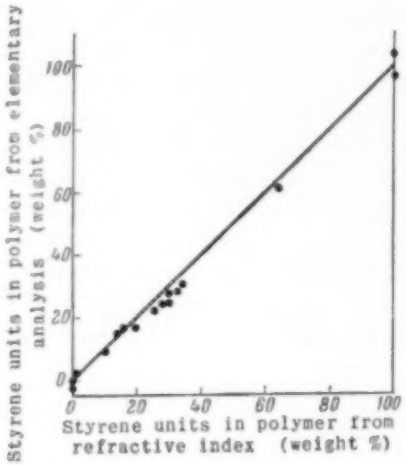

FIG. 7. Results of the determination of the content of styrene units in the polymers by % elementary analysis.

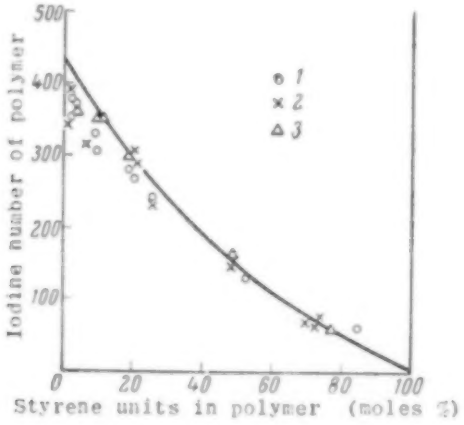

FIG. 8. The iodine numbers of copolymers with various styrene-unit contents. (1) samples of copolymers obtained at 30°; (2) at 40° and (3) at 50°. For plotting the calculated curve the iodine number of polybutadiene was taken as 436.

numbers found are in good agreement with the calculated values (for plotting the curve the iodine number of polybutadiene was taken as 436—the mean value from six determinations—the theoretical iodine number is 470). At low styrene-

contents (up to 20 per cent) the iodine number was a little lower than the calculated value (Fig. 8). This systematic error has the following cause: A low styrene unit content as a rule corresponds to a low degree of conversion and in plotting the curve, and also in calculating the proportion of styrene units from the refractive index we did not apply a correction for the butyl end-groups in the copolymer, from the butyllithium. The two corrections operate in the same direction, hence at a low degree of conversion a systematic deviation on the side of lower iodine numbers is always found.

The proportion of styrene units present in blocks of polystyrene was determined by oxidizing samples of the polymer with tert-butyl hydroperoxide in the presence of osmium tetroxide [9]. Oxidation occurs at the double bonds with the formation of aldehydes. Where styrene units occur between butadiene units comparatively low-molecular dialdehydes are formed that are soluble in alcohol. Styrene units combined in a block remain unchanged. The proportion of block polystyrene is estimated from the weight of the insoluble portion of the oxidation product.

The 1,2 unit content was determined by infrared spectroscopy in the overtone region [12], and the intrinsic viscosity of the polymers was measured in benzene solution at 20 °C.

CONCLUSIONS

In a study of the homopolymerization and copolymerization of butadiene and styrene by butyllithium in benzene the following was established.

(1) Styrene is a more active monomer than butadiene in homopolymerization, the activation energy of the propagation reaction is 12·3 kcal/mole in the first case and 18 kcal/mole in the second.

(2) In copolymerization butadiene reacts preferentially, i. e. the latter has a higher activity than styrene. This "reversal" of activity is cau ed by more favourable steric factors in the interaction of butadiene moleculeswith active centres (the frequency factor is three orders higher than that in the case of styrene).

(3) The apparent copolymerization constants depend on the degree of conversion because the butadiene units in the polymer take part in the formation of active polymerization centres.

(4) The product of the copolymerization constants is equal to unity, i. e. the relative activity of the active centres is independent of the terminal monomer unit.

(5) With high proportions of styrene in the initial mixture the phenomenon of a limiting degree of conversion does not occur; butadiene reacts first at a rate corresponding to that in homopolymerization and the styrene reacts subsequently. As a result of this polymerization sequence a peculiar type of block copolymer is formed, consisting of two blocks—a block of polybutadiene containing a few styrene units, and a block of polystyrene.

Translated by E. O. PHILLIPS

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THE EFFECT OF POLAR ADDITIVES ON THE STEREOSPECIFIC POLYMERIZATION OF PROPYLENE*

G. A. RAZUVAEV, K. S. MINSKER, G. T. FEDOSEEVA and V. K. BYKHOVSKII

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A SHORT time ago we showed that the presence of amines in stereospecific polymerization with a catalyst system consisting of titanium chloride and aluminium triethyl alters the degree of polymerization of the polymers [1] without significantly affecting the ratio of the fractions.

It is of some interest to study the effect on the stereospecific polymerization of propylene by complex catalysts of other classes of nucleophilic compounds containing unshared electron pairs, capable of interacting with both the unoccupied 3 *p* level of the neutral Al atom in aluminium triethyl and with the *d* orbital of titanium trichloride. It has been suggested that these compounds, like the amines [1], will exert an effect on the ratio of the propagation and termination reaction rates. Representative compounds of the following classes were chosen: ethers (dioxan), sulphides (diphenylsulphide) and heterocyclic compounds (pyridine, thianthrene).

The results of experiments on the effect of these compounds on the stereospecific polymerization of propylene are given in Table 1.

TABLE 1. STEREOSPECIFIC POLYMERIZATION OF PROPYLENE

Additive	Additive: $TiCl_3$ (mole/mole)	Molecular wt.	Yield (g)	Additive	Additive: $TiCl_3$ (mole/mole)	Molecular wt.	Yield (g)
—	—	50,000	312	Dioxan	0·85	175,200	323
—	—	53,600	335	Dioxan	1·0	140,000	368
—	—	49,350	287	Dioxan	1·0	125,800	222
—	—	59,840	297	Diphenyl-			
Dioxan	0·05	68,800	297	sulphide	0·15	71,000	334
Dioxan	0·15	72,800	293	,,	0·25	98,400	291
Dioxan	0·35	80,000	—	,,	0·65	98,400	352
Dioxan	0·35	98,400	310	,,	0·85	99,000	340
Dioxan	0·5	130,400	—	Pyridine	0·5	72,800	—
Dioxan	0·5	111,040	270	,,	0·5	75,000	200
Dioxan	0·65	156,000	302	,,	0·6	98,400	—
Dioxan	0·65	130,400	—	Thianthrene	0·15	89,000	280
Dioxan	0·65	156,000	330	,,	0·15	104,800	—

* Vysokomol. soedin. **2**: No. 3, 404–407, 1960.

It is seen that the molecular weight of the polymer increases with increasing ratio of additive:titanium chloride. This agrees with the results obtained when amines were used [1].

The molecular-weight maximum observed at additive:titanium chloride ratios < 1 in the case of dioxan can be explained by the presence of two electron donor atoms in its molecule. Vesely [2] has also reported the effect of increase in the molecular weight of polypropylene by the addition of tributylamine.

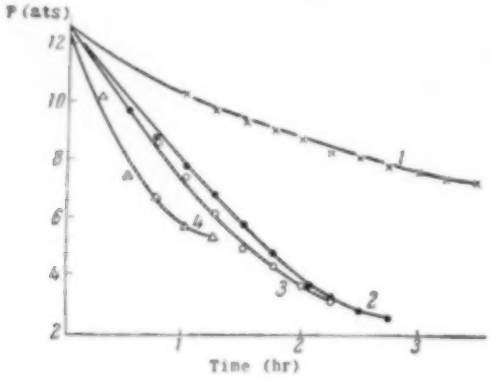

FIG. 1. Variation in rate of stereospecific polymerization of propylene in the presence of dioxan and pyridine (1) without additive, (2) 0·15 mole % dioxan, (3) 0·25 mole % dioxan, (4) 0·5 mole % of pyridine.

Dioxan and pyridine were found to have an accelerating effect on the stereospecific polymerization (diagram), which we did not expect. The apparent rate constants increased by 15 per cent in the presence of 0·15 moles per cent of dioxan, by 25 per cent with 0·25 moles per cent of dioxan and by a factor of about 2·5 in the presence of 0·50 moles per cent of pyridine. These results cannot be explained by the simple radical mechanism of stereospecific polymerization in the presence of complex catalysts formed on mixing metal alkyls with metal chlorides put forward by Nenitescu [3] and supported later by Topchiev and coworkers [4, 5] and by Badin [6].

No theory of stereospecific polymerization has yet been developed that could explain all the experimental facts. However the favourable effect of ether additives (by ethers we mean solvents having a heteroatom with an unshared electron pair) and the essential presence of a metal alkyl and a metal chloride in the reaction mixture enables analogies to be sought with organomagnesium compounds (MgR_2+MgX_2, where X is halogen), the complexes of which with ethers correspond to the composition $MgR_2.MgX_2.2(C_2H_5)_2O$ [7], with complexes of individual organic compounds of metals of Groups I and II of the periodic system, with polymerization in the presence of Alfin catalysts ($CH_2=CH-CH_2$)Na

[10,11] and in all probability, with the reduction by metal hydrides. Michovich and Mikhaelovich [12], in particular, have discussed the analogy of organomagnesium compounds with lithium aluminium hydride, and Talalaeva and Kocheshkov [8] with complexes of metals of Groups I and II of the periodic system.

Reductions with metal hydrides and Grignard reactions take place in ethers and the addition of small quantities of ether to the saturated hydrocarbon medium in Alfin polymerization considerably increases the polymerization rate, though it reduces the degree of crystallinity of the polymers.

One complex of $TiCl_3$ with trimethylamine, of the composition $2(CH_3)_3N.TiCl_3$, is described in the literature [13]. We have shown [1] the possibility of forming complexes of titanium trichloride with aniline, dimethylaniline and triethylamine, both in the presence and absence of aluminium triethyl. This also can be compared with the effect of increase in molecular weight of the polymers formed (and sometimes also the overall rate of the process) in Ziegler-type polymerizations in the presence of ether additives.

Although the detailed mechanism of stereospecific polymerization remains obscure numerous indirect experimental data indicate that the initiation process is connected with the partial transfer of electrons from the catalyst system to the monomer. It may be supposed that when the unsaturated molecules are activated during polymerization the opened-up molecular levels of the bond at which addition takes place take part in the process of combination with the catalyst complex. In this connexion it may be supposed that the catalyst coordinates about itself molecules of the ether-type additive, the unshared electron pair then goes to an advantageous level of the active centre by "displacing" its electron to a higher level. Naturally in these circumstances the transfer of an unpaired electron to the opening orbit of a monomer double bond is facilitated. This should result in a marked increase in molecular weight of the polymer and sometimes in the polymerization rate also.

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EXPERIMENTAL*

Petroleum ether (b.p. 90–105°) was purified in the usual way and stored over metallic sodium. Pyridine was distilled from solid caustic alkali and redistilled. It was again redistilled over metallic sodium before use. Dioxan was purified [14] first by refluxing over lead peroxide and subsequent filtration through a fine filter, and then according to Riechle and Milas [19]. Diphenylsulphide and thianthrene were prepared from benzene and sulphur in the presence of aluminium chloride [15]. The diphenylsulphide, isolated from the benzene layer, was purified by vacuum distillation (b.p. 110–112°/20 mm, $n^{18.5}$ 1·635, in agreement with the literature [16]). The thianthrene was precipitated from benzene by absolute ethanol (m.p. 158–160°, in agreement with the literature [17]).

* T. A. Domracheva took part in the synthetic part of the work.

The experiments on the polymerization of propylene* were carried out by a method similar to that described in reference [1]. The molecular weight of the polypropylene was determined from the intrinsic viscosity in *o*-xylene at 120° according to an approximate equation [18].

CONCLUSIONS

(1) The stereospecific polymerization of polypropylene has been carried out in the presence of a heterogeneous catalyst system based on $TiCl_3 + Al(C_2H_5)_3$.

(2) It is shown that pyridine, dioxan, diphenylsulphide and thianthrene, in certain ratios with respect to the titanium trichloride, increase the molecular weight of the polypropylene. In the presence of pyridine and dioxan an increase in polymerization rate was observed.

Translated by E.O.PHILLIPS

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* The $TiCl_3$ was not subjected to additional activation by grinding before use.

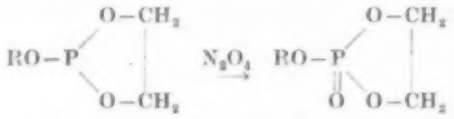
POLYMERS CONTAINING PHOSPHORUS—I. SYNTHESIS AND POLYMERIZATION OF ETHYLENEALKYLPHOSPHATES*

K. A. PETROV, E. E. NIFANT'EV and L. V. FEDORCHUK

(*Received* 14 *December* 1959)

THE ordinary phosphates are well studied compounds, used in industry and in agriculture. However phosphates have not yet been synthesized having a five-membered, cyclic, ether grouping in their composition, nor high-molecular phosphates condensed other than through vinyl ester groups. A simple method is put forward in this paper for the preparation of ethylenealkylphosphates and for their conversion to polymers.

The synthesis of ethylenealkylphosphates was achieved by oxidation of ethylenealkylphosphites, which are available compounds [1]†, with nitrogen dioxide:



$R = C_3H_7$; C_4H_9; *iso*-C_4H_9; C_5H_{11}; C_6H_{13}; C_6H_5

Experiment showed that the best yield of the phosphates was obtained when oxidation was carried out without solvent at -5 to $+5°$, with subsequent displacement of the oxides of nitrogen by dry nitrogen, and distillation of the product immediately after oxidation. When the material was allowed to stand for a long time at room temperature and then distilled, considerable resinification occurred. Evidence on the structure of these compounds was obtained from the infrared spectrum of ethylenepropylphosphate. The spectrum has an intense absorption band at a frequency of 1286 cm^{-1} which corresponds to the vibration of the P=O bond and appears in phosphates in the 1300—1275 cm^{-1} region [2]. The compound in question cannot be the isomeric propylvinylphosphoric acid, the formation of which on distillation might be suggested, because there is no band in the spectrum in the 1850 and 1650 cm^{-1} regions, characteristic of the double bond, or a band at 2700 cm^{-1} corresponding to the P—OH group [2].

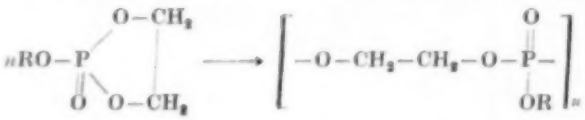
We used these cyclic phosphates for the preparation of phosphorus-containing polymers. It has been shown previously that ethylenephosphonates form poly-

* Vysokomol. soedin. **2**: No. 3, 417–420, 1960.

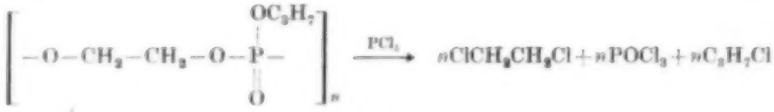
† Two of the phosphates ($R = C_6H_{13}$ and C_6H_5) were prepared for the first time by us, by the interaction of ethylenechlorophosphite with hexanol and phenol.

meric products with a degree of polymerization of 3–4 on heating in sealed tubes [3]. We found that the cyclic phosphates (in contrast to phosphonates) form products of higher molecular weight (degree of polymerization, 10–14) on polymerizing under the same conditions. The polymers obtained were of approximately the same molecular weight, and had the same properties, in experiments with and without a catalyst (sodium).

The macromolecular phosphates are neutral substances. In structure they belong to the class of polyesters, formed as a result of the opening of the cyclic phosphates:



When the polymers are treated with phosphorus pentachloride, phosphorus oxychloride, dichloroethane and the corresponding alkyl chloride are formed, for example:



The macromolecular phosphates described in this communication can be used as plasticizers.

EXPERIMENTAL

Ethylenehexylphosphite. 300 ml of absolute ether, 126·5 g (1 mole) of ethylenechlorophosphite and 152 g (1·5 moles) of triethylamine were placed in a three-necked flask fitted with a reflux condenser, stirrer and dropping funnel. 102 g (1 mole) of hexyl alcohol was then added dropwise, with stirring, to the flask cooled in ice-water. The reaction mixture was allowed to stand for 10–15 hours, filtered and again allowed to stand for the same period. After a second filtration the ether was distilled from the mother liquor and the residual oil distilled *in vacuo*. After a second distillation 143 g (72% of theory) of ethylenehexylphosphite was obtained; b.p. 115–118°/13 mm; n_D^{20} 1·4480; d_4^{20} 1·1090; $MR_{D\,\text{found}}$ 46·70; $MR_{D\,\text{calc.}}$ 46·72.

$C_{18}H_{17}PO_3$	Found %:	*P* 16·07
	Calculated %:	*P* 16·14

Ethylenephenylphosphite. As described above, 148 g (85 per cent of theory) of ethylenephenylphosphite was obtained from 126·5 g of ethylenechlorophosphite, 152 g of triethylamine and 96 g of phenol; b.p. 133–135°/13 mm; n_D^{20} 1·5350; d_4^{20} 1·2225; $MR_{D\,\text{found}}$ 49·22; $MR_{D\,\text{calc.}}$ 49·19.

$C_8H_9PO_3$	Found %:	*P* 16·20
	Calculated %:	*P* 16·84

According to the literature [4], b.p. 73°/0·3 mm, n_D^{20} 1·5342.

Ethylenealkylphosphates. The phosphite was placed in a four-necked flask, protected from moisture and fitted with a stirrer, thermometer and capillary gas inlet, and nitrogen peroxide in a current of dry nitrogen was passed through. The rate at which the gases were passed was such that the temperature of the reaction mixture did not exceed 0°. At the end of the reaction (appearance of a green colour) the excess of oxide of nitrogen was swept out by a current of dry nitrogen and the product was twice distilled *in vacuo* at 0·4 mm. The experimental results are shown in Table 1, where R is the radical in the formula

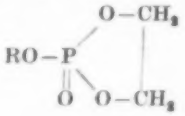


TABLE 1. SYNTHESIS OF ETHYLENEALKYLPHOSPHATES

R	Yield (%)	Boiling point (°C) at 0·4 mm Hg	n_D^{20}	d_4^{20}	MR_D		Phosphorus content %	
					Found	Calculated	Found	Calculated
C_3H_7	62·7	103–104	1·4297	1·2020	36·65	35·65	18·58	18·67
C_4H_9	70·0	115–116	1·4330	1·1850	39·48	39·70	16·84	17·22
iso-C_4H_9	76·6	110–111	1·4310	1·1740	39·48	39·70	16·96	17·22
C_5H_{11}	55·0	123·5–124	1·4345	1·1410	44·34	44·32	16·61	15·98
C_6H_{13}	83·0	137–138·5	1·4361	1·1160	49·20	48·94	14·78	14·90
C_6H_5	53·0	149–150·5 (melting point 29°)	—	—	—	—	15·15	15·50

Polymerization of ethylenealkylphosphates. Polymerization was carried out by heating in sealed tubes in an atmosphere of nitrogen. In some experiments a catalyst (sodium) to the extent of 1% by weight of the phosphate, was used. The polymer from ethylenepropylphosphate was obtained after standing for three months in an atmosphere of nitrogen. The polymers were soluble in benzene, chloroform and carbon tetrachloride, and insoluble in water, alcohol and ether. The viscosity of 1·5 per cent solutions of the polymers in benzene at 20° was measured. Data on the polymers are shown in Table 2.

Reaction of polyethylenepropylphosphate with phosphorus pentachloride. 3·2 g of phosphorus pentachloride was added in portions to 0·84 g of the polymer in 3 ml of dry carbon tetrachloride, with stirring and cooling in ice-water. The mixture was then stirred for a further two hours at 35°. Unreacted phosphorus pentachloride was removed by passing sulphur dioxide through the mixture which was then distilled. The following fractions were obtained: I b.p. 44–46°; II b.p. 69–78°; III b.p. 82–84°; IV b.p. 100–107°.

TABLE 2. CONDITIONS OF POLYMERIZATION OF ETHYLENEALKYLPHOSPHATES AND PROPERTIES OF THE POLYMERS

Basic unit	Reaction time (hr)	Temperature (°C)	Catalyst	η_{sp}^{20}	Molecular weight
$C_2H_5OP(O)O-CH_2-CH_2-O-$	10	140	Na	0·186	2320
	4 months	20	—	0·14	2090
	10	140	—	0·15	2280
$C_4H_9-OP(O)OCH_2CH_2-O-$	10	140	—	0·192	2320
$C_5H_{11}OP(O)OCH_2CH-O-$	10	140	—	0·23	2420
	10	140	Na	0·31	2950

Fraction I after redistillation had b.p. 45–46°, n_D^{20} 1·3869 and consisted of propyl chloride. According to the literature [5], b.p. 46·4°; n_D^{20} 1·3873.

Fraction III after redistillation had b.p. 83–84°, n_D^{20} 1·4426 and consisted of 1,2-dichloroethane. According to the literature [5], b.p. 83·7°, n_D^{20} 1·4431.

Fraction IV after redistillation had b.p. 103–106° and was phosphorus oxychloride. According to the literature [5], b.p. 105·7°.

CONCLUSIONS

(1) A synthesis of ethylenealkylphosphates by oxidation of ethylenealkylphosphites with nitrogen peroxide has been developed.

(2) It is shown that the ethylenealkylphosphates polymerize on prolonged standing or on heating. The structure of the products is discussed.

Translated by E. O. PHILLIPS

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LETTERS TO THE EDITOR

CHEMILUMINESCENCE IN THE SOLVENT AND PHASE BOUNDARY PRODUCTION OF NYLON*

S. G. ENTELIS, V. IA. SHLIAPINTOKH, O. N. KARPUKHIN and O. V. NESTEROV

(*Received 5 November* 1959)

WE have observed that the polycondensation of hexamethylenediamine with adipyl dichloride is accompanied by chemiluminescence. The experiments were carried out at room temperature. The luminescence arises on mixing solutions of hexamethylenediamine (saturated solution) and adipyl dichloride (0·23 mole/l.) in toluene. Chemiluminescense also occurs on carrying out the reaction at the phase boundary when a toluene solution of the acid chloride (0·23 mole/l.) is poured into an aqueous solution of hexamethylenediamine (0·5 mole/l.).

The luminescence was recorded by means of an FEU-29 photo-multiplier, sensitive in the region 350–610 mμ. According to the results obtained the intensity of luminescence was greater than 10^6–10^7 photons per second from 1 cm^3 of reactor.

Control experiments showed that the luminescence is connected with the polycondensation process itself, and not with crystallization of the polymer formed or with the reaction of a product (hydrogen chloride) with the diamine.

This phenomenon opens up new possibilities in the investigation of the kinetics and mechanism of polycondensation reactions and can obviously be used for the purpose of control of the technological processes of polymer production.

Translated by E. O. PHILLIPS

* Vysokomol. soedin. **2**: No. 3, 463, 1960.

GRAFT COPOLYMERIZATION OF METHYL METHACRYLATE AND STYRENE ON TO GELATIN INDUCED BY IONIZING RADIATION*

L. KISS and IA. DOBO

(*Received* 15 *December* 1959)

WE have studied the grafting of methyl methacrylate and styrene on to gelatin by the action of small total dosages of ionizing radiation, with intermittent irradiation and low radiation intensity. A Wenger X-ray apparatus of the "Stabil-250" type and a ^{60}Co preparation of activity 60 curies was used as the radiation source. In some experiments the films were irradiated in the presence of water. The presence of traces of water promoted better swelling of the film in the monomer and hence the penetration of the monomer into the film.

Irradiation was carried out at 25° in glass ampoules in the absence of oxygen. After irradiation the grafted films were extracted for 24 hours with acetone in the case of methyl methacrylate and benzene in the case of styrene. The extent of grafting was determined gravimetrically. The grafted films were treated with distilled water at 80° for 12 hours to remove unchanged gelatin.

The experimental results are given in Table 1.

TABLE 1. GRAFTING OF METHYLMETHACRYLATE AND STYRENE ON GELATIN

Strength of dose (r/h)	Period of irradiation (min)	y*	Wt. loss after treatment of film water (%)	Strength of dose (r/h)	Period of irradiation (min)	y*	Wt. loss after treatment of film with water (%)
43,500	60	27·8	3·6	15,500	3600	4·42	8·5
22,300	60	15·5	3·5	16,300	3600	3·65	8·7
43,500	40	12·1	1·3	16,300	3600	4·22	8·6
22,300	40	8·7	10·5				

$y = P/P_0 - 1$, where P – is the weight after grafting, and P_0 – is the original weight.

* Vysokomol. soedin. **2**: No. 3, 464–465, 1960.

Table 1 shows that at low total dosages a fairly high degree of grafting on to gelatin can be achieved in the case of methyl methacrylate and rather less in the case of styrene.

The structure of the graft copolymers of gelatin with styrene and methyl methacrylate and their thermal properties are being studied.

Translated by E. O. PHILLIPS

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ABSTRACTS FROM PAPERS PUBLISHED IN *VYSOKOMOLEKULIARNYE SOEDINENIIA* Vol. 2, No. 1, 1960*

MECHANISM OF THE DECOMPOSITION OF ALIPHATIC-AROMATIC TRIAZENES UNDER THE INFLUENCE OF ACIDS AND WATER

L. V. Alferova, B. A. Dolgoplosk and V. A. Kropachev, Vysokomol. soedin. **2**: No. 1, 3–12, 1960

A KINETIC study has been made of the decomposition of aliphatic-aromatic tri-acid and the activation energy has been determined.

The interaction of aliphatic-aromatic triazenes with water and acids proceeds according to an ionic mechanism with the formation of aniline, nitrogen, alcohol or the corresponding ester and unsaturated hydrocarbon.

Partial isomerization of the alkyl groups leading to the formation of iso-alcohols and esters is observed.

Decomposition of the triazenes in neutral aqueous emulsion media at elevated temperatures proceeds both by the ionic and radical mechanisms simultaneously.

THE SYNTHESIS OF VINYL COMPOUNDS OF LEAD AND A STUDY OF THEIR POLYMERIZATION

V. V. Korshak, A. M. Polyakova and M. D. Suchkova, Vysokomol. soedin. **2**: No. 1, 13–19, 1960.

TRIETHYLVINYL lead and diethyldivinyl lead have been synthesized and their polymerizing capacity has been investigated.

The compounds have been found to be very unstable and to decompose under the action of peroxides at 120–130° with the liberation of metallic lead.

Copolymerization products of triethylvinyl lead with styrene and α-methylstyrene have been obtained.

ON THE HIGH ELASTICITY DEFORMATION LAW OF NETWORK POLYMERS

G. M. Bartenev and T. N. Khazanovich, Vysokomol. soedin. **2**: No. 1, 20–28 1960.

EMPIRICAL formulas have been proposed for the relation between the stress and high elasticity deformations of network polymers (rubbers) and have been tested at various kinds of stressed states of the rubbers. The single-parameter formula agrees with the experimental data much better than other known formulas of this type (within the range of 40–60 per cent elongation). The region of validity of the two-parameter formula is 200–300 per cent elongation. Other known two-parameter formulas give considerable deviation from experimental results. A two-parameter formula has also been proposed that can be used to described small deformations of welled network polymers (up to 40–60 per cent elongation).

* English Abstracts reprinted from Vysokomol. soedin. **2**: No. 1, 1960.

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NUMERICAL EXPRESSION OF THE MOLECULAR WEIGHT DISTRIBUTION OF POLYMERS

B. E. Geller and I. M. Meskin, Vysokomol. soedin. **2**: No. 1, 29–34, 1960.

THE generalized shape of the differential curve for the molecular weight distribution of polymers has been examined and it has been proposed to employ the "reduced degree of homogeneity" to characterize such distribution. By the reduced degree of homogeneity is meant the ratio between the measured and maximum possible degrees of polydispersity. This is calculated from the ratio between the sum of the square heights of the curve and the square sum of its heights multiplied by the number of steps of differentiation. The ratio between the degree of homogeneity and the mean molecular weights characterizes the "reduced degree of homogeneity". A relation has been shown to exist between this quantity and the physico-mechanical properties of the polymer.

DEFORMATION PROPERTIES OF POLYMERS

E. E. Glukhov, A. A. Gorina and A. V. Shelion, Vysokomol. soedin. **2**: No. 1, 38–45, 1960.

A THEORETICAL analysis has been presented of the constants contained in the equation describing the initial portion of the creep curve. A correlation has been established between these constants and the polymer structure. Experiments have been described, confirming the theoretical inferences. The latter have been shown to be of practical interest.

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APPLICATION OT FHE ULTRASONIC METHOD IN THE QUANTITATIVE DETERMINATION OF THE COMPONENTS OF POLYETHYLENE-POLYPROPYLENE MIXTURES AND OF ETHYLENE-PROPYLENE COPOLYMERS

S. P. Kabin and O. G. Usyarov, Vysokomol. soedin. **2**: No. 1, 46–50, 1960.

IN the paper the results are presented of a study of the mechanical losses occurring at 2 mHz longitudinal ultrasonic vibrations in polyethylene-polypropylene mixtures and ethylene-propylene copolymers with various concentrations of the components. For polyethylene-polypropylene mixtures within the temperature range of −60 to 80° C two regions of mechanical relaxation losses, characteristic of each of the components, are observed at −60 and −45° C. The magnitude of the losses is proportional to the concentration of the respective component. For the copolymer, relaxation losses take place in a single region at about 7° C. The losses in this region are proportional to the propylene concentration within the limits ranging from 0 to 40 per cent. From the nature of the temperature dependence of the mechanical losses one may judge whether the material is a mixture or polymer. From the magnitude of the losses in this region one may quantitatively estimate the composition of the copolymerization products.

ADHESION OF HIGH POLYMERS—V. ADHESION OF SYNTHETIC RUBBERS TO VARIOUS HIGH MOLECULAR SUBSTRATES

S. S. Voyutskii and V. L. Vakula, Vysokomol. soedin. **2**: No. 1, 51–60, 1960

THE adhesion of a number of synthetic rubbers to various high molecular substrates has been determined by means of a specially developed method based on the separation of the elastomers brought into contact.

The effect of the chemical composition and structure of the rubber-like adhesives and high molecular substrates (size, shape and polarity of the macromolecules, phase state of the polymer) on the adhesion has been shown. The temperature influence on the latter

has also been investigated and it has been found that a rise in temperature mostly leads to increased adhesion. The relative part played by the individual factors determining diffusion may change significantly.

The results of the investigation have been interpreted in terms of the diffusion theory of adhesion being developed by the authors.

ON HETEROCHAIN POLYESTERS—XXVI. A STUDY OF SOME LAWS GOVERNING POLYESTERIFICATION AT THE INTERFACE BOUNDARY

V. V. Korshak, S. V. Vinogradova and A. S. Lebedeva, Vysokomol. soedin. **2**: No. 1, 61–66, 1960.

A STUDY has been made of the influence of various factors: stirring intensity, solution concentration, nature of the solvent, rate and order of addittion of the reagents and reaction temperature on the yield and reduced viscosity of the polyester of diane and *iso*phthalic acid obtained on polycondensation at the interface boundary. The highest molecular weight of the polyester for concentrated solutions of the reagents was obtained on adding in about 11 minutes at 20° C a solution of isophthalyl chloride in *p*-xylene to an aqueous alkaline solution of diane phenolate (concentration of the solution 0·1 M), the reaction mass being mixed with a stirrer. The possible reactions during polyesterification at the interface boundary have been examined.

A STUDY OF THE DECOMPOSITION OF DIAZOAMINOBENZENE IN HYDROCARBON MEDIA UNDER THE INFLUENCE OF ORGANIC ACIDS AND THE USE OF THE REACTION TO INITIATE POLYMERIZATION

L. V. Alferova, B. A. Dolgoplosk and V. A. Kropachev, Vysokomol. soedin. **2**: No. 1, 67–74, 1960.

THE decomposition of diazoaminobenzene in hydrocarbon media under the influence of benzoic acid has been shown to lead to almost quantitative formation of aniline and nitrogen and regeneration of benzoic acid.

Based on a study of the composition of the products formed under varying conditions, in particular in the presence of free radical acceptors, a discussion has been presented of the mechanism of the process. It has been shown that the mechanism markedly differs from that underlying the decomposition of fatty-aromatic triazenes.

CARBOCHAIN POLYMERS AND COPOLYMERS—XX. ON THE POLYMERIZATION AND COPOLYMERIZATION OF 1-FLUORO-1,1-DICHLORO- AND 1,1-DIFLUORO-1-CHLOROPROPYLENES 2

H. S. Kolesnikov and N. G. Matveeva, Vysokomol. soedin. **2**: No. 1, 82–84: 1960.

1-FLUORO-1, 1-DICHLORO- and 1,1-dichloro-1-fluoro-propylenes have been synthesized and their polymers and copolymers with methylmethacrylate and styrene have been obtained. The styrene copolymer has been found to have a glass temperature of ~100°, i. e. higher than that for the homopolymers. The elevated glass temperature may be explained by formation of hydrogen fluoride bonds between the polymer chains.

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EFFECT OF POLYDISPERSITY ON THE LIGHT SCATTERING OF POLYMER SOLUTIONS

Yu. Ya. Kolbovskii, Vysokomol. soedin. **2**: No. 1, 85–87, 1960.

THE angular distribution of light scattering for polydisperse Gaussian coils has been calculated for the case of polymers obtained by radical polymerization in the absence of secondary effects (Bresler-Frenkel molecular weight distribution).

It has been shown that the light scattering method may be employed not only for determining the intrinsic sizes of the molecules, but for calculating the ratio between recombination and all other chain terminating mechanisms.

UPGRADING OF COTTON CORD BY MEANS OF OZONIZATION

Kh. U. Usmanov, V. A. Kargin, B. I. Aikhodzhaev and I. Sh . Inoyatov, Vysokomol. soedin. **2**: No. 1, 88–91, 1960.

A STUDY has been made of the action of ozone on the physico-mechanical properties of cord from mean-filament cotton fiber of the grade 108-F and of the possibility of its upgrading.

It has been shown that during ozonization of the cord, decomposition of the fats and waxes of the cotton fibre takes place, as well as a noticeable improvement in the strength of the cord. On subsequently washing the ozonized cord with water at 25° C complete removal of the fats and waxes (at 25° C) takes place as well as a marked increase in the cord strength. The method is the most economical when the ozonization is applied at the wet twisting stage of the cord manufacture.

POLYCONDENSATION IN THE SOLID PHASE—III. POLYCONDENSATION OF *P*-AMINOALKYLPHENYL-ALKANECARBOXYLIC ACIDS IN THE SOLID PHASE

A. V. Volokhina, M. N. Bogdanov and G. I. Kudryavtsev, Vysokomol. soedin. **2**: No. 1, 92–96, 1960.

THE policondensation of six *p*-aminoalkylphenylalkanecarboxylic acids in relation to their chemical structure, in particular to the number of methylene groups in the molecule, has been studied by means of continuous weight measurements during the polycondensation process and by determining the amounts of water evolved. It has been found that in the series of *p*-aminoethylphenylakanecarboxylic acids there are quite definite relationships between the initial temperature of polycondensation, the range between the initial polycondensation temperature and the melting points of the amino acids, the temperature coefficient of the polycondensation rate, the effective activation energy of the reaction in the solid phase, and the number of methylene groups in the amino acid molecules and as well as the melting point.

THE VULCANIZING ACTION OF DI-OXYDIETHYLENETHIURAMDISULPHIDE

M. S. Feldshtein, I. I.Eitingon and B. A. Dogadkin, Vysokomol. soedin. **2**: No. 1, 97–102, 1960.

DI-OXYDIETHYLENETHIURAMDISULPHIDE was shown to be an effective accelerator and active vulcanization agent of butadiene-styrene and natural rubber mixtures. In comparison with tetramethylthiuramdisulfide it leads to a lower vulcanization rate in the initial stages of the process. An analogous effect is achieved on using zinc N-oxydiethylenedithiocarbamate instead of zinc dimethyl dithiocarbamate as vulcanization accelerator.

INVESTIGATION INTO THE MECHANICAL PROPERTIES OF POLYMERS UNDERGOING IRRADIATION—I. THE STRENGTH AND ULTIMATE FORCED ELASTICITY OF SOLID POLYMERS IN THE PROCESS OF IRRADIATION IN A NUCLEAR REACTOR

M. A. Mokulshii, Yu. S. Lazurkin, M. B. Fiveiskii and V. I. Kozin, Vysokomol. soedin. **2**: no. 1, 103–109, 1960.

THIS study has been devoted to an investigation into the mechanical properties of materials being irradiated in a nuclear reactor. A description has been made of the apparatus for the measurement of the strength, yield value and the creep of the materials. The strength of polymethylmethacrylate and the ultimate forced elasticity of polyvinylchloride have been determined. A reversible decrease in the values of these quantities under irradiation has been revealed.

INVESTIGATION INTO THE MECHANICAL PROPERTIES OF POLYMERS UNDERGOING IRRADIATION—II. CREEP OF SOLID POLYMERS AND RUBBERS IN THE PROCESS OF IRRADIATION IN A NUCLEAR REACTOR

M. A. Mokulshii, Yu. S. Lazurkin and M. B. Fiveiskii, Vysokomol. soedin. **2**: No. 1, 110–118, 1960.

IN the paper the results are presented of experiments on the creep of various polymers during irradiation. As in the case of strength and ultimate forced elasticity measurements, reversible change in the mechanical properties has been revealed. The rate of creep increases sharply in the process of irradiation and falls after its termination.

SYNTHESIS OF POLYESTERS FROM DINITRILES AND GLYCOLS VIA POLYIMINOESTER HYDROCHLORIDES

E. N. Zilberman and N. M. Teplyakov, Vysokomol. soedin. **2**: No. 1, 133 -135 1960.

FURTHER data have been obtained on the conditions for carrying out the synthesis of polyesters from the dinitriles of dicarboxylic acids and glycols by way of the hydrochlorides of polyiminoesters. With the aid of this method polyesters of molecular weight from 1000 to 1700 have been obtained from the dinitriles of adipic, azelaic, sebacic and *p*-phenyleneacetic acids and ethylene glycol, butanediol and diethylene glycol.

POLYTITANOMETHYLSILOXANES AND POLYTITANOETHYLSILOXANES

K. A. Andrianov and E. Z. Asnovich, Vysokomol. soedin. **2**: No. 1, 136–140, 1960.

NEW polytitanoorganosiloxanes with methyl and ethyl groups at the silicon atom have been obtained by means of a double decomposition reaction. The elementary composition and the infrared absorption spectra of the polymers have been determined.

Polytitanomethylsiloxane and polytitanoethylsiloxane have been found to be readily soluble in organic solvents and not to melt at 500° and higher. Based on the elementary composition, infra-red absorption data and the properties of the new polytitanoorganosiloxanes a linear-cyclic structure of the polymer molecules has been proposed.

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KINETICS OF THE EMULSION POLYMERIZATION OF STYRENE

G. D. Berezhnoi, P. M. Khomikovskii and S. S. Medvedev, Vysokomol. soedin. **2**: No. 1, 141–152, 1960.

THE effect of the nature and concentration of initiators, the concentration of the emulsifier and the temperature on the rate of the emulsion polymerization of styrene and on the mean molecular weights of the polymers has been investigated. The dependence of the overall rate of the reaction on the emulsifier concentration has been shown to be determined by the topochemistry of formation of the primary radicals (in the aqueous solution or on the surface of the polymer particles) and upon the concentration of the initiator, and is determined by two types of termination of the molecular chains (interaction with one another and with the primary radicals). The overall activation energy of the polymerization reaction lies within the limits of 14–16 kcal/mole.

The experimental results have been subjected to quantitative treatment, based on the concept that latex polymerization is a homogenous process with the emulsifier of mean concentration and with account made of the two types of polymer chain termination.

SYNTHESIS OF SULPHUR-CONTAINING ARYLALIPHATIC POLYAMIDES AND STUDIES OF THE PROPERTIES OF MEMBERS OF THE SERIES

O. Ya. Fedotova and A. B. Shapiro, Vysokomol. soedin. **2**: No. 1, 153–157, 1960.

THE synthesis has been carried out for the first time of six sulphur-containing arylaliphatic polyamides and a description has been made of their properties. The kinetics of the synthetic reactions have also been determined. An activity series for the diamines in the polycondensation reaction as well as the dependence between structure and properties in the series of sulphur-containing aliphatic polyamides have been established. A plasticizing effect of the -S- and -S-S-groups located between the aromatic radicals in the polyamide chain has also been found to exist.

COMPARISON OF THE PROPERTIES OF POLYMERS WITH POLYSILOXANE AND PHENYLENESILOXANE CHAINS IN THE MOLECULES

K. A. Andrianov, V. E. Nikitenkov and N. N. Sokolov, Vysokomol. soedin. **2**: No. 1, 158–161, 1960.

POLYORGANOSILOXANES have been synthesized, in the primary chain of which 50 per cent of the oxygen has been substituted by phenylene radicals. Among such polymers a low molecular phenylsiloxane with 8 Si atoms and 6 OH groups has been obtained.

Polyorganophenylenesiloxanes have been shown to possess a higher thermal stability and a lower thermal elasticity than the corresponding polyorganosiloxanes.

PLASTICIZATION OF POLYVINYL ALCOHOL-STYRENE AND POLYACRYLIC ACID-STYRENE GRAFT COPOLYMERS

V. A. Kargin, N. A. Plate and V. P. Shibaev, Vysokomol. soedin. **2**: No. 1, 166–173, 1960.

A STUDY has been made of the plasticizing action of tetralin and glycerine on polyvinyl alcohol-polystyrene and polyacrylic acid-polystyrene graft copolymers. It has been shown that the separate action of the polar and non-polar plasticizer can be realized on each of the components of the copolymer. Tetralin plasticizes only the polystyrene parts of the chain and shifts the respective transition temperature in accordance with the partial volume rule, whereas glycerol acts primarily on the polar groups of polyvinyl alcohol and polyacrylic acid. When jointly present the plasticizers supplement and intensify each others action.

In the polyvinyl alcohol-styrene graft copolymers with 48 per cent polystyrene content a definite structural ordering characteristic of polyvinyl alcohol is maintained. The properties (thermomechanical, structural, plasticizability) of graft copolymers in the condensed state are feasibly explained on assuming the existence in the system of polymer microregions where chain segments of the same chemical nature are accumulated.

ON THE PAPER BY B. A. DOGADKIN AND V. A. SHERSHNEV "THE REACTION OF TETRAMETHYLTHIURUM DISULPHIDE WITH RUBBER AND WITH COMPOUNDS WITH A LABILE HYDROGEN ATOM"

S. E. Bresler, B. A. Dogadkin, E. N. Kazbekov, E. M. Saminskii and V. A. Shershnev, Vysokomol. soedin. **2**: No. 1, 174, 1960.

THE conclusions as to the source of the electron resonance spectrum appearing in the process of rubber vulcanization by thiuram (1) are not final. The spectrum is similar to that given by copper compounds present as impurities in the rubber-MTD mixtures. However in order for the spectrum to appear double bonds or labile hydrogen must be present in the vulcanization mixture.

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ABSTRACTS FROM PAPERS PUBLISHED IN *VYSOKOMOLEKULIARNYE SOEDINENIIA* Vol. 2, No. 2, 1960*

α-METHYLSTYRENE-BUTADIENE COPOLYMERS WITH PREDOMINANT VINYL COMONOMER CONTENT

Ya. N. Prokofiev, M. I. Farberov and V. A. Shadricheva, Vysokomol. soedin. **2**: No. 2, 185–192, 1960.

EXPERIMENTAL data on the copolymerization kinetics of α-methylstyrene and butadiene have been presented. It was found that polymerization ceases after consumption of the butadiene and a more precise method of calculating this "polymerization limit" has been proposed. The copolymer composition has been calculated both with the aid of the basic equation as well as of the approximate equation proposed by Soviet authors. The calculations agree satisfactorily with experimental results. The possibility of obtaining α-methylstyrene-butadiene copolymers by the compensation method has been calculated and it has been shown that owing to the predominant low concentration of butadiene in the polymerizing mixture the method is difficult to apply.

ACOUSTIC BIREFRINGENCE IN A CONDENSED (LIQUID) POLYMER

V. E. Eskin, Vysokomol. soedin. **2**: No. 2, 193–196, 1960.

THE acoustic and dynamic birefringence in condensed polybutadiene of molecular weight 3500 have been measured. The calculated orientation relaxation time of the macromolecules has been used to estimate their sizes. The result agrees within an order of magnitude with calculation based on the statistical theory.

THE MOLECULAR WEIGHT OF CARBOCHAIN POLYMERS AS FUNCTION OF DISPERSITY RESULTING FROM MECHANICAL DISPERSION

N. K. Baramboim and V. N. Gorodilov, Vysokomol. soedin. **2**: No. 2, 197–199, 1960.

POWDERED vibrodispersion products of polystyrene and polymethylmethacrylate have been separated into fractions of varying dispersity. Viscometric molecular weight determinations have revealed the existence of a correlation between the molecular weight and the particle dispersity.

FILLED POLYMERS—I. THE FILLING OF POLYMETHYLMETHACRYLATE WITH AMINATED BENTONITE ADDED DIRECTLY TO THE MONOMER

I. A. Uskov, Vysokomol. soedin. **2**: No. 2, 200–204, 1960.

THE addition of highly dispersed octadecylammonium bentonite to a methylmethacrylate medium leads on polymerization to a new type of filled polymer. The polymer is characterized by enhanced hardness, exceeding the non-filled material by 23 per cent and by a rise in the transition temperature from the viscoelastic state to viscous flow, i. e. by a broader temperature region of visco-elastic deformation.

* English abstracts reprinted from Vysokomol. soedin. **2**: No. 2, 1960.

RELATION BETWEEN THE MOLECULAR WEIGHT OF POLYETHYLENETEREPHTHALATE AND THE VISCOSITY OF ITS SOLUTIONS IN PHENOL-DICHLOROETHANE MIXTURES

E. V. Kuznetsov, A. O. Vizel, I. M. Shermergorn and S. S. Tyulenev, Vysokomol. soedin. **2**: No. 2, 205–209, 1960.

A NEW solvent of polyethyleneterephthalate dissolving the latter at room temperature has been proposed. The k' coefficient of Huggin's equation for concentration dependence was found equal to 0·42.

The empirical coefficients k and α of the Staudinger-Mark equation have been determined ($k = 0{\cdot}92 \times 10^{-4}$, $\alpha = 0{\cdot}8$). The equation assumes the following form: $[\eta] = 0{\cdot}92 \times 10^{-4} M^{0{\cdot}85}$ or $M = 61200\,[\eta]^{1{\cdot}18}$.

EQUILIBRIUM SEDIMENTATION OF HYBRID POLYMERS IN THE DENSITY GRADIENT

S. E. Bresler, L. M. Pyrkov and S. Ya. Frenkel, Vysokomol. soedin. **2**: No. 2. 216–220, 1960.

IT has been shown that ultracentrifugation in a density gradient may be used to analyze the composition and molecular weight distribution of block and graft polymers. An original modification of Meselson's method has been developed, in accordance with which by selection of a proper solvent the hybrid polymer accumulates as a band in the central part of the sedimentation cell and the corresponding homopolymers (when they are present) give the Boltzman distribution at the bottom and at the meniscus. With the aid of the new method preliminary data have been obtained on the composition of styrene-isoprene block polymers synthesized by the "live chain" method.

STUDIES ON DIFFUSION PROCESSES IN POLYMERS—I. DIFFUSION OF MONOATOMIC GASES THROUGH POLYMER FILMS OF DIFFERENT STRUCTURE

N. S. Tikhomirova, Yu. M. Malinskii and V. L. Karpov, Vysokomol. soedin. **2**: No. 2, 221–229, 1960.

THE diffusion of helium and argon through polyethylene, polyvinylchloride, polyamide 54/10, methylolpolyamide 2/10, polytetrafluoroethylene and butadiene—30 per cent styrene (SKS-30) has been studied at various temperatures with the aid of Daynes' manometric method.

The assumption that the diffusion constants of argon diminish in value with growing intermolecular interaction has been confirmed. The diffusion constants D have been shown to fall with increase in the packing coefficient of the polymer chains.

The lowest diffusion constants of argon and the highest activation energy of diffusion are observed with polyamides and polytetrafluoroethylene.

The polymers are arranged in the following order with respect to the magnitude of increase of ΔH and ΔS: polytetrafluoroethylene, SKS-30, methylolpolyamide 2/10, polyamide 54/10, polyethylene, polyvinylchloride.

The ΔH and ΔS values of dissolution of the gas in the polymer may serve as qualitative characteristic of the degree of flexibility of the chains.

STUDIES ON DIFFUSION PROCESSES IN POLYMERS—II. THE EFFECT OF THE ATOMIC DIAMETER ON GASEOUS DIFFUSION IN THE POLYMER

N. S. Tikhomirova, Yu. M. Malinskii and V. L. Karpov, Vysokomol. soedin. **2**: No. 2, 230–237, 1960.

A STUDY has been made of the diffusion of He, Ar, Ne, Xe through polyethylene and polyamide 54/10 at various temperatures.

The diffusion constants (D) and the activation energy of diffusion (E_D) of these gases depend upon their atomic diameters. An increase in the latter by 1·43Å causes a fourfold decrease in D and twofold increase in E_D. The enthalpy and entropy of solution increase in parallel with increase in atomic diameter of the gas.

The relation between the heat of solution and the atomic diameter of the gas is expressed by the following empirical equations: $H = 3{\cdot}9d - 3{\cdot}8$ for polyethylene, $H = 5{\cdot}0d - 7{\cdot}4$ for polyamide 54/10.

It was shown by extrapolation that there is a temperature region in which the dependence of the solubility of monoatomic gases in the polymer upon the diameter reverses. For polyethylene this occurs at minus 10–0°, for the polyamide 54/10 at 115–117° C.

ON THE NATURE OF THE "STATISTICAL" FRICTION OF RUBBER-LIKE POLYMERS

G. M. Bartenev and V. V. Lavrentev, Vysokomol. soedin. **2**: No. 2, 238–242, 1960

In the paper it has been stressed that actually no-one has measured the static friction of rubber. The reason for this has been analyzed and a method has been proposed for measuring friction at the beginning of shear, free from shortcomings of previous studies. The results of measurements have been presented, from which it follows that static friction, determined as the friction coefficient at the beginning of slip, is conditional since it depends upon the accuracy of the displacement determination and upon the rate of tangential stress application.

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THE ACTION OF ULTRASONIC WAVES ON AQUEOUS SOLUTIONS OF Na-CARBOXY METHYLCELLULOSE

I. E. Elpiner and N. I. Pyshkina, Vysokomol. soedin. **2**: No. 2, 243–246, 1960.

In the present study it has been shown that under the action of ultrasonic waves Na-carboxymethylcellulose in aqueous solution undergoes various chemical changes. The type of change depends upon the nature of the gas present in the irradiated solution. In the presence of oxygen the polymer was found to yield stable degradation products. In such cases the viscosity of the irradiated solution and molecular weight of the polymer were observed to decrease and the hydration of the latter to increase. Other changes occur on irradiation of the solution in the presence of hydrogen, in general increase in molecular weight and decrease in hydration being found to take place. At the same time there is a fall instead of rise in solution viscosity. This indicates that increase in the molecular weight of Na-carboxymethylcellulose in the presence of hydrogen is accompanied by a decrease in asymmetry of the molecule.

The phenomena observed are discussed in terms of mechano-chemical conceptions.

THE ACTION OF DOUBLE SYSTEMS OF VULCANIZATION ACCELERATORS—II. CHEMICAL INTERACTION OF ACCELERATORS AND THE ACTIVATING MECHANISM OF DOUBLE SYSTEMS

B. A. Dogadkin, M. S. Feldshtein and E. N. Belyaeva, Vysokomol. soedin. **2**. No. 2, 247–258, 1960.

From data on the vulcanization of various types of rubbers it has been found that double systems of accelerators may be divided into three classes: (a) systems with mutual activation of the accelerators, (b) systems with activation of one of the accelerators and (c) systems with additive action of the accelerators. The vulcanization kinetics of the first two classes of accelerators (non-additive action) are characterized by a lag in the initial stages and sharp acceleration in the main period of the process. On the interaction of accelerators of which one contains a benzothiazolyl group and the other is a hydrogen donor 2-mercapto-

benzothiazol has been observed to form. The latter also forms on interaction of the accelerators in the rubber medium, the yield being significantly higher in that case, than on separate action of the accelerators on the rubber. The introduction of sulphur to the mix increases the yield of 2-mercaptobenzothiazol. The activity of double accelerator systems is the greater the more intensive the formation of 2-mercaptobenzothiazol. The mutual activation of the accelerators is explained by the formation of an intermediate complex, decomposing into free radicals that induce that reaction of sulphur with rubber and polymerization of the latter.

THE LIGHT SCATTERING AND VISCOSITY OF DICHLOROSUBSTITUTED POLYSTYRENE IN AN IDEAL SOLVENT—I. POLY-2,5-DICHLOROSTYRENE

V. E. Eskin and K. Z. Gumargalieva, Vysokomol. soedin. **2**: No. 2, 265–271, 1960.

THE light scattering and viscosity of 8 polydichlorostyrene fractions (M ranging from $0{\cdot}5 \times 10^6$ to 13×10^6) in an ideal solvent have been measured. The molecular weights and unperturbed coil sizes have been determined. The latter exceed only insignificantly ($\approx 5\%$) the size of polystyrene coils of equal degree of polymerization. The dependence of $[\eta]$ and h_0^{-2} upon M is that holding in general for non-flowing Gaussian coils.

INVESTIGATION OF THE SPHERULITE STRUCTURE OF POLYMERS—II. MACROSPHERULITES OF POLYMERS

P. V. Kozlov, M. I. Iovleva and Li Pan-Tun, Vysokomol. soedin. **2**: No. 2, 284–286, 1960.

USING polyethylenesebacate as example it has been shown that polymers obtained from solutions in or near the region of phase separation may form macrospherulites. From polyethylenesebacate dissolved in furfuralcohol macrospherulites of diameter up to 0·4 cm were obtained on maintaining at room temperature.

Preliminary investigation of such spherulites revealed a high crystalline ordering of the molecular chains, the absence of an amorphous phase in them and a characteristic picture of their degradation both along the surfaces and the radii, from the apex of the hemispheres to the sides and centres.

DIELECTRIC PROPERTIES OF SOME POLYESTERS WITH AROMATIC NUCLEI IN THEIR CHAINS

G. P. Mikhailov and M. P. Eidelnant, Vysokomol. soedin. **2**: No. 2, 287–294, 1960

IN the investigation the temperature-frequency relation of the angle of dielectric losses and of the dielectric constant of four polyesters, namely, dianterephthalate, dianisopthalate diancarbonate and diansebacate has been presented.

In all the polysters there are two regions where $tg\delta$ passes through a maximum. The losses belong either to the dipole-radical or to the dipole-elastic types.

The dipole radical losses have been shown to be due to relaxation of the ester groups.

The time of relaxation of dipole-radical losses or the temperatures of the region $tg\delta_{max}$ depends mainly upon the chemical structure of the acid.

The relaxation time of dipole-elastic losses has been found to increase with the aromatic nuclei in the polyester. Polydiancarbonate, polydianisophthalate and polydianterephthalate are crystallizing polymers.

INVESTIGATION INTO THE TEMPERATURE-FREQUENCY RELATIONSHIPS OF THE ANGLE OF DIELECTRIC LOSSES OF MIXED POLYESTERS

G. P. Mikhailov and M. P. Eidelnant, Vysokomol. soedin. **2**: No. 2, 295–302, 1960.

THE temperature-frequency relations of the angle of dielectric losses for a number of mixed polyesters of aromatic and aliphatic acids have been investigated.

Two regions of dipole-radical losses corresponding to the two acids and one region of dipole-elastic losses have been found for all the polyesters. The temperature of maximum $tg\delta$ of the dipole-elastic losses is determined by the concentration of the polyester component.

The capacity for crystallization of the mixed polyesters of which one component does not crystallize increases with increase in concentration of the crystallizing component in the polyester. When the crystallizing component cantains more aromatic nuclei than the non-crystallizing component an increase in the degree of crystallinity may lead to a fall in the temperature of maximum $tg\delta$ of the dipole-elastic losses.

EFFECT OF PRESSURE ON THE COHESION OF POLYPROPYLENE

Yu. V. Ovchinnikov, K. S. Minsker and L. A. Igonin, Vysokomol. soedin. **2**: No. 2, 306–309, 1960.

THE conditions for the formation of transparent specimens on the compression molding of polypropylene powders over a large range of temperatures and pressures have been investigated,

Whatever the pressure no intergrowth of the polymer particles with the disappearance of physical boundaries between them takes place at temperatures below the melting point of polypropylene ($T_{m} = 169°C$).

The formation of transparent articles is possible in the temperature and pressure regions bounded by the upper branch of the pressure-temperature curve. The region is above the polypropylene melting temperature.

The application of high pressures raises the melting temperature.

Articles molded at 200°C and pressures above the upper limit (above the limit of formation of opaque materials) posses inferior physico-mechanical properties as compared with those formed at pressures below this limit.

ON THE EXPRESSION FOR THE RESILIENCE POTENTIAL OF STRAINED RUBBER IN THE NON-EQUILIBRIUM STATE

L. S. Priss, Vysokomol. soedin. **2**: No. 2, 313, 1960.

THE reasons are given for the deviation between the expressions for the resilience potential of rubber in the non-equilibrium state obtained by the author and by Mooney. A method for the experimental testing of one of the fundamental principles underlying the theory has been proposed. This consists in measuring the change in the resilience potential with time in the initial period after deformation of the rubber.

CYCLIC COPOLYMERIZATION OF DIVINYLACETAL AND VINYL MONOMERS

S. G. Matsoyan, M. N. Avetyan and M. G. Voskanyan, Vysokomol. soedin. **2**: No. 2, 14, 1960.

THE possibility of cyclic copolymerization has been studied in the cases of divinylbutyral with styrene and vinyl acetate. The copolymers formed are soluble in benzene, chloroform and acetone and do not contain double bonds.

ABSTRACTS FROM PAPERS PUBLISHED IN *VYSOKOMOLEKULIARNYE SOEDINENIIA* Vol. 2, No. 3, 1960*

MECHANISM OF OXIDATION OF CELLULOSE AND OF ITS APPROXIMATE MODELS BY ATMOSPHERIC OXYGEN

O. P. Golova, N. S. Mayat and E. A. Andrievskaya, Vysokomol. soedin. **2**: No. 3, 337–340, 1960.

THE oxidation of cellulose and of the approximate models of its structural units, and methylglucosides, by atmospheric oxygen has been investigated.

It has been shown that α and β methylglucosides are highly stable towards the action of oxygen at 85–86° for 1–70 hours in alkaline media. Highly pure cellulose with insignificant carbonyl content is sufficiently stable towards the action of molecular oxygen in alkaline medium.

It has been suggested that a chain-radical mechanism underlies the oxidation of cellulose and of its models, a long induction period prevailing.

SYNTHESIS OF NEW CELLULOSE AND OTHER POLYSACCHARIDE DERIVATIVES—V. SYNTHESIS OF CELLULOSE PHENOLATES AND INVESTIGATION OF THEIR PROPERTIES

Z. A. Rogovin and T. V. Vladimirova, Vysokomol. soedin. **2**: No. 3, 341–346 1960.

A METHOD has been developed for synthesis of cellulose phenolates by exchange interaction of cellulose tosylates with sodium phenolate solution. The cellulose phenolate obtained had a value of $\gamma = 75$. It was shown that the primary alcohol group was the first to participate in the reaction.

Mixed cellulose phenyltosylates of a higher degree of substitution ($\gamma = 150$–190) were obtained.

The solubility of cellulose phenolates of different degrees of substitution has been investigated, as well as their stability towards various factors.

By nitration of a relatively little substituted cellulose phenolate mixed cellulose esters with nitric acid and dinitrophenol have been obtained. The properties of these cellulose esters have been investigated.

SOME PHYSICO-CHEMICAL CHARACTERISTICS OF HIGH MOLECULAR POLYACRYLAMIDE

V. G. Aldoshin, M. N. Savitskaya and S. Ya. Frenkel, Vysokomol. soedin. **2**: No. 3, 347–353, 1960.

A HIGH molecular weight polyacrylamide used as coagulant and structurizer of soil has been investigated with the aid of three physico-chemical methods, namely viscometry, light scattering and sedimentation in the ultracentrifuge; formamide, distilled water and 10% NaCl being used as solvents. The molecular weight of the specimen studied was $(5{\cdot}5 \pm 0{\cdot}3) \times 10^6$. In all three solvents its molecules had the statistical coil configuration usual for linear polymers.

* English abstracts reprinted from Vysokomol. soedin. **2**: No. 3, 1960

It was shown that owing to partial hydrolysis of its amide groups polyacrylamide is a polyelectrolyte. Evidently from this stems its high solubility in water. From its reduced viscosity in distilled water it follows that the degree of hydrolysis (i. e. the effective degree of ionization) of polyacrylamide is not very large.

A number of practical suggestions have been given for estimating the quality of the technical product in the process laboratory.

MOLECULAR INTERACTION IN POLYMER SOLUTIONS—II. THE THIRD VIRIAL COEFFICIENT OF SOLUTIONS OF FLEXIBLE MACROMOLECULAR CHAINS

Yu. E. Eisner, Vysokomol. soedin. **2**: No. 3, 360–364, 1960.

THE third virial coefficient of linear macromolecules in the region of the Flory point has been calculated within the framework of the "pearl necklace" model. The results obtained have been compared with the theories of Stockmayer-Casassa and Kawai based on the "smoothened density" model.

SYNTHESIS AND POLYMERIZATION OF ARYLPHOSPHONITRILES AND ALKYLPHOSPHONITRILES

V. V. Korshak, I. A. Gribova, T. V. Artamonova and A. N. Bushmarina, Vysokomol. soedin. **2**: No. 3, 377–385, 1960.

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THE reaction of diaryl- and dialkylphosphotrichlorides and ammonium chloride in organic solvents has been investigated. Various products have been shown to form, depending upon the conditions of the reaction. At 175°C and with excess ammonium chloride octaphenyltetraphosphonitrile is formed. Based on the results obtained views have been expressed as to the reaction mechanism.

The polymerization of the phosphonitrile derivatives has been studied over the temperature range 320–500°C on the example of octaphenyltetraphosphonitrils. Under these conditions a mixture of tri-, penta- and hexamers is obtained, as well as a product insoluble in organic solvents and softening at 350–450°C.

INVESTIGATION INTO THE POSSIBILITY OF PREPARING UNSATURATED COMPOUNDS OF CELLULOSE BY THE CHUGAEV REACTION

A. I. Polyakov, V. A. Derevitskaya and Z. A. Rogovin, Vysokomol. soedin. **2** No. 3, 386–389, 1960.

PRELIMINARY studies have been made to ascertain the possibility of obtaining unsaturated cellulose compounds by the thermal degradation of the cellulose-xanthogenic acid derivatives, the dixanthogenide and methylxanthogenate.

It has been shown that the degradation of the derivatives proceeds according to the mechanism proposed by Chugaev.

GEOMETRY OF LINEAR POLYMERS—VII. THE INFLUENCE OF VOLUME EFFECTS ON THE SHAPE OF MACROMOLECULES IN SOLUTION

O. B. Ptitsyn, Vysokomol. soedin. **2**: No. 3, 390–396, 1960.

THE influence of volume effects on the shape of macromolecules in solution was investigated by means of the statistical method developed earlier. It was shown that near the Θ-point the end-to-end distance of the polymer chain increases somewhat more rapidly than the distance between the middle point of the chain and the end-to-end vector, but this effect is very small. From a discussion of the relationship between the flow birefringence of poly-

mer solutions and the optical anisotropy of molecules it follows that the influence on the former of factors changing the shape of the macromolecules can be approximately evaluated by the ellipsoid theory as proposed by Tsvetkov and Frisman. The volume effects cause a small but not negligible increase of the dynamo-optic constant. Near the Θ-point this increase is 25 per cent of the increase in the linear size of the chains.

ON THE RELATION BETWEEN THE STATIC BREAKDOWN AND DEFORMATION OF SOLID AMORPHOUS POLYMERS

M. I. Bessonov and E. V. Kuvshinskii, Vysokomol. soedin. **2**: No. 3, 397–403 1960.

It has been shown that the creep rate and breaking time of solid polymers may be correlated by means of empirical equations that, as in the case of metals, may be of practical importance.

A marked difference has been indicated between the effects of stress and temperature on the rate of deformation and of breaking and cases have been shown where in general there is no connexion between the two.

It has been noted that to elucidate the physical nature of the relation between strain and breakdown, other, more sensitive characteristics are required than the macroscopic rates of these processes.

SYNTHESIS AND POLYMERIZATION OF 3-VINYL-2,5-DIPHENYLFURAN

N. A. Adrova and M. M. Koton, Vysokomol. soedin. **2**: No. 3, 408–410, 1960.

3-Vinyl-2,5-diphenylfuran has been obtained for the first time and its block and solution polymerization has investigated. Complication of the vinylfuran molecule by the addition of two phenyl groups in the 2,5 position leads to an increase in the polymerization rate and to an elevated softening temperature of the polymer.

THE SYNTHESIS AND BASIC PROPERTIES OF POLYACRYLATE ESTERS OF DIFFERENT DEGREES OF POLYMERIZATION

A. A. Berlin, T. Ya. Kefeli, Yu. M. Filippovskaya and Yu. M. Sivergin, Vysokomol. soedin **2**: No. 3, 411–416, 1960.

The effect of methacrylic acid doses in the reaction of condensation telomerization has been studied with respect to the degree of polymerization, the composition and the properties of the polyacrylate esters as well as of their rate of three-dimensional polymerization.

Lowering the amount of methacrylic acid below that required for obtaining monomers with the ultimate degree of chain termination leads to the formation of crosslinking oligomers with degree of polymerization above 1.

The following new polyacrylate esters have been synthesized by the method of condensation telomerization:

dimethacrylate-poly-(diethyleneglycol phthalates) with degree of polymerization $n = 2$, 4, 8 and 20;

dimethacrylate (*bis*-ethyleneglycol) thiodivalerate, dimethacrylate (*bis*-diethyleneglycol) thiovalerate and dimethacrylate (bis-triethyleneglycol) thiodivalerate;

dimethacrylate (*bis*-diethyleneglycol) sulfodivalerate.

The visco-liquid oligomers synthesized are capable of homopolymerization and copolymerization with a number of unsaturated monomers.

STUDIES IN THE SPHERULITE STRUCTURE OF POLYMERS—III. A STUDY OF THE MICROSPHERULITE STRUCTURE OF POLYMERS BY ETCHING

P. V. Kozlov, N. F. Bakeev, Li Pan-Tun and A. S. Kaftanova, Vysokomol soedin. **2**: No. 3, 421–426, 1960.

WITH the aid of an etching technique optical and electron miscroscopic studies were made of the structure of microspherulites formed in polyethylenesebacate films when the latter were obtained from solutions.

In the polyethylenesebacate microspherulites both crystalline and amorphous phases were found to coexist separately. The crystalline phase is a helical ribbon packet of polymer chains constituting the structural elements of the microspherulite proper. The amorphous phase constitutes globular formations not connected with the structural elements.

INVESTIGATION IN ORGANOPHOSPHORUS POLYMERS—IX. THE POLYCONDENSATION OF PHOSPHINYL DICHLORIDES WITH DIOXY COMPOUNDS

V. V. Korshak, I. A. Gribova and M. A. Andreeva, Vysokomol. soedin. **2**: No. 3, 427–432, 1960.

THE polycondensation of phosphinyl dichlorides with hydroquinone in nitrobenzene solution and with diethylene glycol in dichloroethane was investigated. The duration and the temperature of the reaction were found to affect the yield and intrinsic viscosity of the polyester. The degree of the reaction considerably increases with rise in temperature and in concentration of the reactants.

The kinetics of the polycondensation were obtained by following the evolution of hydrogen chloride in the process of the reaction.

PLASTICIZATION OF ACRYLIC ACID-STYRENE BLOCK POLYMERS

V. A. Kargin, V. A. Kabanov, N. A. Plate and N. P. Pavluchenko, Vysokomol. soedin. **2**: No. 3, 433–440, 1960.

BLOCK copolymers of acrylic acid and acrylic acid-styrene copolymer and of acrylic acid and styrene have been obtained by the method of interface boundary polymerization and a study has been made of their plasticization by glycerine and tetraline both individually and in combination.

The thermomechanical properties of the plasticized block polymers could be satisfactorily explained by assuming the presence in them of polystyrene-(ged) or acrylic acid-(ged) enriched microregions. This is supported by the fact that polar and non-polar plasticizers have a selective action on the polar and non-polar components of the block copolymers.

REACTION OF AROMATIC DIAMINES WITH UREA AND ITS THIO-DERIVATIVES

V. D. Yasnopolskii and E. A. Krasnoselskaya, Vysokomol. soedin. **2**: No. 3, 441–443, 1960.

WHEN in the reaction of hexamethylenediamine with urea the former is replaced by *p*- and *m*-phenylenediamines, i.e. by diamines having the same number of carbon atoms but a cyclic structure, polymers are produced in the form of non-fusible powders of poor solubility in organic solvents. They are readily soluble in sulphuric acid and somewhat less in pyridine.

When attempts were made to obtain polymers from thiourea and *p*-phenylenediamine decomposition took place with the formation of ammonia and hydrogen sulphide. The yield of polymer which had the form of a black non-fusible powder and was insoluble in organic solvents was very small.

On interaction of diphenylthiourea with *p*-phenylenediamine a resinous product was obtained, softening at 87°C. The polymer could be drawn out in the heated state, to black fibres, becoming brittle on cooling.

MEASUREMENT OF THE DENSITY OF POLYMERS BY THE ELECTROMAGNETIC FLOAT METHOD

M. Kozler, E. Z. Fainberg and N. V. Mikhailov, Vysokomol. soedin. **2**: No. 3, 446–450, 1960.

In the paper a detailed examination has been made of the characteristic features of measuring the density of liquids and solids by means of the electromagnetic float method.

The method has been shown to be applicable to polymers both in the dry and moist states.

CARBOCHAIN POLYMERS AND COPOLYMERS—XXI. COPOLYMERS ON THE BASIS OF BICYCLO-(2,2,1)-HEPTADIENE-2,5 AND 1,2,3,4,7,7-HEXACHLOROBICYCLO-(2,2,1)-HEPTADIENE-2,5

H. S. Kolesnikov, A. P. Suprun, T. A. Soboleva, A. F. Plate, G. L. Slonimskii M. A. Pryanishnikova and G. A. Tarasova, Vysokomol. soedin. **2**: No. 3, 451–455, 1960.

The copolymers of bicyclo-(2,2,1)-heptadiene-2,5 with 1,2,3,4,7,7-hexachlorobicyclo-(2,2,1)-heptadiene-2,5, with styrene and with vinylacetate have been synthesized for the first time. Investigation of the products showed that the bicycloheptadienehexachlorobicycloheptadiene copolymers (Mole percentage ratio 70-5:29-5) are readily soluble in dichloroethane and toluene and exhibit high elasticity at elevated temperatures (250–350°C). The bicycloheptadiene-vinylacetate copolymer also has a wide temperature range of high elasticity (60 to 350°C).

SYNTHESIS OF NEW CELLULOSE AND OTHER POLYSACCHARIDE DERIVATIVES—VI. SYNTHESIS OF THE ESTERS OF CELLULOSE AND CHLOROALKANE ACIDS.

Chang Wei-Kang and Z. A. Rogovin, Vysokomol. soedin. **2**: No. 3, 456–462, 1960.

The possibility of utilizing chloroalkane acids for the synthesis of new types of cellulose esters has been explored. A new class of mixed esters of cellulose and acetic and chloroalkane acids with varying amounts of chloroalkane acid residues has been synthesized. Also the synthesis was performed of another new class of cellulose esters with high amounts of chloroalkane substituents (chlorovaleric and chloroenanthic acids).

The influence of various factors on the composition of the resultant ester has been studied.

POTENTIOMETRIC TITRATION AND THE CONFORMATIONS OF ISO- AND SYNDIOTACTIC POLYELECTROLYTES

O. B. Ptitsyn, Vysokomol. soedin. **2**: No. 3, 463–464, 1960.

A theoretical treatment of the interaction of closely spaced charged groups in polyelectrolyte molecules with account made of the conformations of their monomer units showed that in polyelectrolytes of the type $(-CH_2-CHR-)_n$ potentiometric titration curves should be steeper for the syndiotactic than for the isotactic forms. Moreover the interaction should lead to an increase in size of the isotactic and a diminution in size of the syndiotactic molecules.

PAPERS FROM *VYSOKOMOLEKULIARNYE SOEDINENIIA* TO BE PUBLISHED IN FULL IN FUTURE ISSUES OF *POLYMER SCIENCE: U.S.S.R.*

A. S. Novikov, V. L. Karpov, F. A. Galil-Ogly, N. A. Slovokhotova and T. N. Dyumayeva: Investigation of the effect of ionizing radiation on the chemical structure of rubber-like, fluorine-containing polymers

V. V. Korshak, S. V. Vinogradova and V. S. Artemova: Investigations in the field of co-ordination-chain polymers—II. Some polymers of quinizarin with metals

V. V. Korshak, S. V. Vinogradova and T. M. Babchintser: Investigations in the field of co-ordination polymers—III. Co-ordination polymers based on *bis*-(8-hydroxyquinolyl) methane

V. K. Bykhovskii and K. S. Minsker: The role of surface electron defects in heterogeneous catalytic polymerization—I. Alfin-type polymerization

K. S. Minsker and V. K. Bykhovskii: The role of surface electron defects in heterogeneous catalytic polymerization—II. Catalyst systems of the Ziegler–Natta type

V. A. Kargin and I. Yu. Marchenko: The glass temperature of crystalline polymers

N. V. Mikhailov, L. G. Tokareva and M. V. Kovaleva: Investigation of the mechanism of ageing or synthetic fibres—I. A study of the thermal and thermal-oxidation reactions of polyamides and polyamide fibres

G. P. Mikhaelov and T. I. Borisova: Investigation of dielectric loss and polarization in stereoregular polymethylmethacrylate

T. M. Birshtein and O. B. Ptitsyn: The conformation, dimensions and dipole moments of syndiotactic macromolecules

V. A. Kargin, V. A. Kabanov and V. P. Zubov: The formation of isotactic polymethylmethacrylate during photopolymerization in the system methyl methacrylate–zinc chloride

S. Ya. Frenkel': The hydrodynamic average molecular weights and criteria of polydispersity of unfractionated polymers

Yu. V. Mitin, Yu. N. Sazanov, G. P. Vlasov and M. M. Koton: Polymerization of dialdehydes

A. A. Berlin, B. I. Liogon'kii and V. P. Parini: The preparation and properties of some aromatic polymers

V. N. Tsvetkov and I. N. Shtennikova: Flow birefringence of poly-*para*-tert-butylphenylmethacrylate—II. The region of high velocity gradients

Z. S. Yegorova, Yu. M. Malinskii, V. L. Karpov, A. E. Kalmanson and L. A. Blyumenfel'd: Chemical changes in polyvinylchloride under the influence of ionizing radiation

S. S. Medvedev, A. D. Abkin, P. M. Khomikovskii, G. N. Gerasimov, V. F. Gromov, Yu. A. Chikin, V. A. Tsingister, A. L. Auer, M. K. Yakovleva, L. P. Mezhirova, A. V. Matveyeva and Z. G. Bezzubik: The polymerization of ethylene by γ-radiation

O. Ya. Fedotova and Mao Bin-Tsyuan': The polycondensation of some 4,4′-dialkylamine-3,3′-dimethyldiphenylmethanes with sebacic acid

Abstracts of papers published in *Vysokomolekuliarnye soedineniia*

Papers to be published in future issues of *Polymer Science: U.S.S.R.*

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INVESTIGATION OF THE EFFECT OF IONIZING RADIATION ON THE CHEMICAL STRUCTURE OF RUBBER-LIKE, FLUORINE-CONTAINING POLYMERS*

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WHEN the fluorine-containing plastics, polytetrafluorethylene and polytrifluorochlorethylene, are subjected to ionizing radiation intensive degradation of the macromolecules occurs, with the formation in the polymer of double bonds and oxygen-containing groups [1, 2].

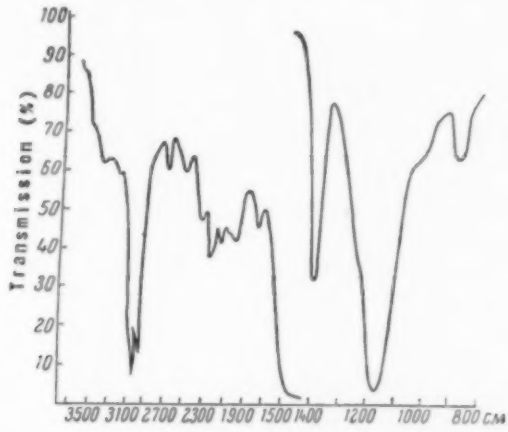

FIG. 1. Infrared spectrum of the fluorine-containing copolymer SKF-32 ($d = 150\mu$).

There is no information in the foreign or Russian literature on the transformations of rubber-like copolymers containing fluorine, of the type of Kel-F and Viton-A, under the action of ionizing radiation.

In a few papers [3–5] there is information on the production from rubber-like fluorine-containing copolymers of rubbers with improved technical properties, by radiation vulcanization. This can be taken as an indication that in contrast to polytetrafluorethylene and polytrifluorochlorethylene, rubber-like fluorine-containing copolymers crosslink under the action of ionizing radiation.

* Vysokomol. soedin. **2**: No. 4, 485–491, 1960.

However the chemical changes that take place in these copolymers on irradiation are not known.

The present communication is devoted to a study of the chemical changes taking place in SKF-32 on irradiation.

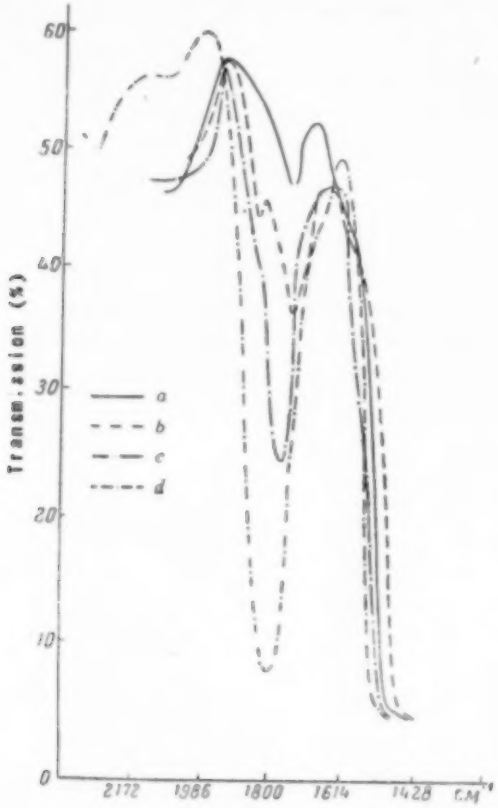

FIG. 2. Infrared spectra of SKF-32 before irradiation and after irradiation in air ($d = 120\mu$). (a) before irradiation; (b) radiation dosage 10×10^6; (c) 20×10^6; (d) 68×10^6 r.

^{60}Co-sources, of activity 1400 and 21,000 g-equiv of radium, were used. The radiation intensity was $0{\cdot}54 \times 10^6$ r/hr. The total dosage of absorbed energy on irradiation was $3\text{–}80 \times 10^6$ r.

Films of the copolymer were irradiated in air and *in vacuo*. The residual pressure in irradiations in the absence of air was 10^{-4} mm.

The chemical changes taking place in the copolymer were followed by infrared spectroscopy. The infrared spectra were plotted with an IKS-14 (double-beam type) spectrometer in the wavelength region from 2·8 to 20μ.

The film thickness for measurements in the 500–1450 cm^{-1} region was 4μ and in the 1450–3500 cm^{-1} region, 140–150μ.

In the spectrum of the original copolymer (Fig. 1) there is a strong, broad band in the 1175–1200 cm^{-1} region corresponding to the C—F bond, strong bands in the 3000–3030 cm^{-1} and 1390–1420 cm^{-1} regions corresponding to the valency and deformation frequencies of the C—H bond, and a band in the 900–910 cm^{-1} region corresponding to the C—Cl bond. The weak band at 1740 cm^{-1} corresponds to terminal $-CH=CF_2$ double bonds or to double bonds within the chain, $R-CF=CF-R$, and also to oxygen-containing groups [6–8]. In the spectrum of the copolymer irradiated in air there are considerable changes, in comparison with the unirradiated polymer, in the 1700–1800 cm^{-1} region. In place of the weak band at 1740 cm^{-1} a strong band appears at 1800 cm^{-1} and a weak band in the 1840 cm^{-1} region. On increasing the radiation dosage the strong band at 1800 cm^{-1} increases considerably and the band at 1840 cm^{-1} disappears. In the 1800 cm^{-1} region there are absorption bands characteristic of oxygen-containing groups joined to fluoro-hydrocarbon radicals, and also to double bonds of the $-CF=CF_2$ type. In the regions of the bands corresponding to the stretching frequencies of the C—H, C—F and C—Cl bonds a reduction in strength of these bands is observed after irradiation, indicating that during irradiation gaseous products including hydrogen, fluorine and chlorine are formed (Fig. 3).

At higher radiation dosages, of the order of 68×10^6 r a band appears in the 2500–2670 cm^{-1} region. At the same time there is a considerable broadening of the contour of the bands in the 2700–3400 cm^{-1} region, which may be taken to indicate the appearance of hydroxyl groups in the fluoro-hydrocarbon chain. The appearance of hydroxyl groups can be explained by the interaction of free polymeric radicals, formed during irradiation, with water vapour in the air. The nature of the infrared spectra of the fluorine-containing copolymer irradiated *in vacuo* differs to some extent from that of the copolymer irradiated in air (Fig. 4).

On irradiating the copolymer *in vacuo* at low dosages of 10×10^6 and 20×10^6 r three bands appear at 1640, 1740 and 1840 cm^{-1}. The band at 1640 cm^{-1} corresponds to double bonds with one fluorine substituent, $-CH=CF-$, the band at 1740 cm^{-1} is characteristic of double bonds of the type $-CH=CF_2$ and of those within the chain, $R-CF=CF-R$.

Interpretation of the third band at 1840 cm^{-1} is very difficult because there is no indication in the literature of oxygen-free groups that absorb in this region. Most probably this band corresponds to the $-CF=CF_2$ bond. The absorption band corresponding to this group in the spectra of various fluorine-containing copolymers lies in the region from 1780 to 1830 cm^{-1} [6]. Possibly the interval is wider than this.

From this it may be deduced that terminal bonds of two types, $-CH=CF_2$ (1740 cm^{-1}) and $-CF=CF_2$ (1840 cm^{-1}), are formed in the copolymer on irradiation *in vacuo*.

On increasing the radiation dosage, absorption in the 1740 cm^{-1} region decreases and in place of two bands (1740 and 1840 cm^{-1}) there is a stronger and

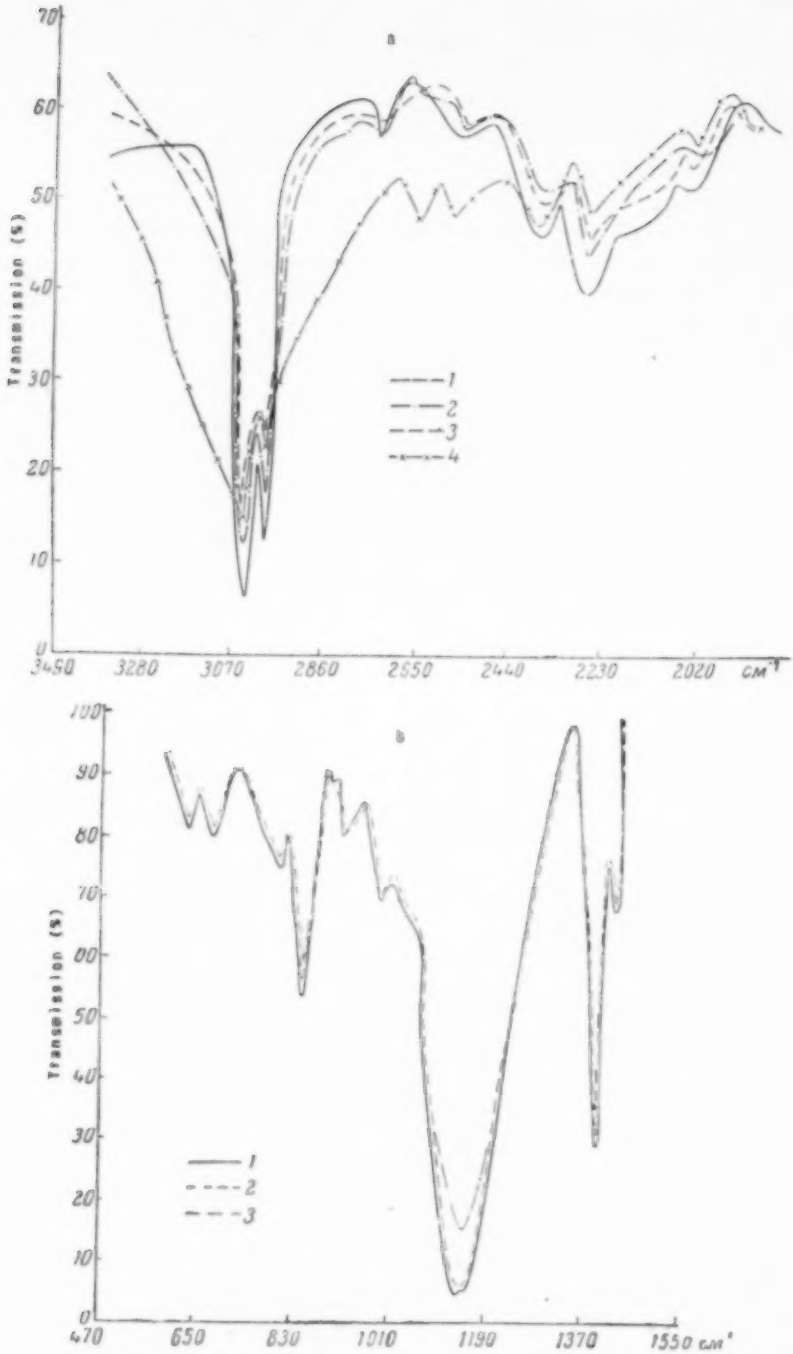

FIG. 3. Infrared spectra of SKF-32 before irradiation and after irradiation in air: a–d = 130 μ; b–d = 3μ. (a) (1) before irradiation; (2) radiation dosage 13×10^6; (3) 20×10^6; (4) 68×10^6 r. (b) (1) before irradiation; (2) radiation dosage 10×10^6; (3) 25×10^6 r.

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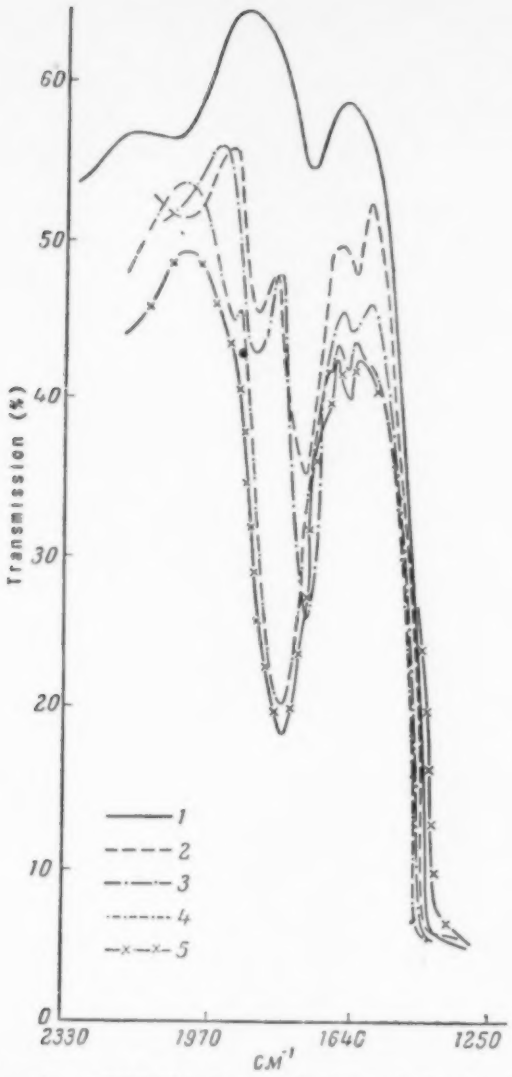

FIG. 4. Infrared spectra of SKF-32 before irradiation and after irradiation *in vacuo* ($d = 130\mu$). (1) before irradiation; (2) radiation dosage 10×10^6; (3) 20×10^6; (4) 30×10^6; (5) 40×10^6 r.

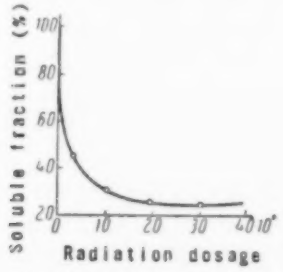

FIG. 5. Variation in solubility of the fluorine-containing copolymer.

broader band with a maximum in the 1800 cm^{-1} region. The decrease in absorption in the 1740 cm^{-1} region indicates that some of the double bonds formed on irradiation react to form crosslinks on further irradiation.

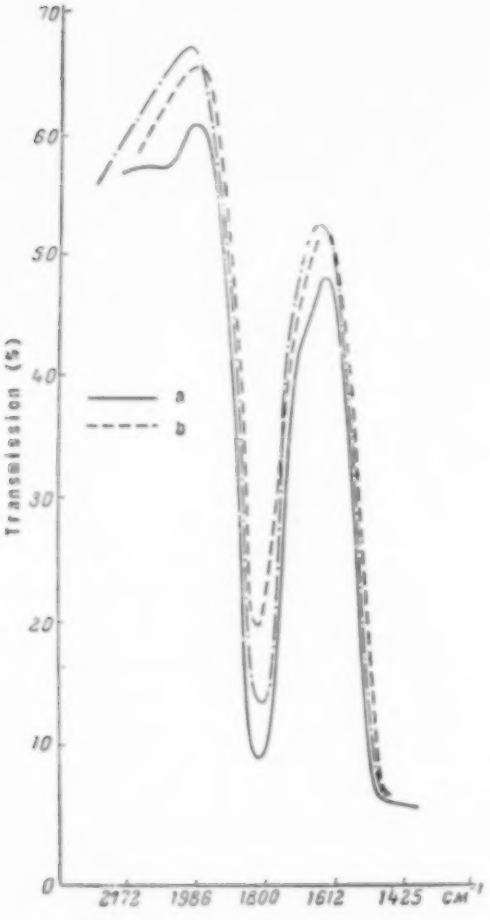

FIG. 6. Infrared spectra of SKF-32 with various vinylidene fluoride contents. Radiation dosage 50×10^6 r. (a) greatest, (b) least vinylidene fluoride content.

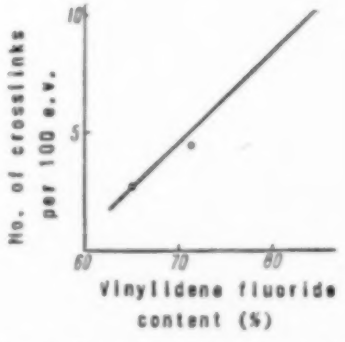

FIG. 7. Dependence of the number of crosslinks formed per 100 eV on the vinylidene fluoride content.

At the same time further formation of double bonds of the $-CF=CF_2$ type takes place, as indicated by the increase in absorption in the 1800 cm^{-1} region. The relatively greater width of this band suggests that on increasing the dosage different lengths of chains associated with double bonds are formed.

A changed in the solubility of the copolymer in methylethylketone after irradiation showed that crosslinking is the predominant process taking place (Fig. 5). The increase in the content of vinylidene fluoride in the copolymer

facilitates the predominance of crosslinking processes (Fig. 6). If the equilibrium modulus is determined for the irradiated copolymer with a Polyani apparatus at a temperature of 150° and the number of crosslinks per 100 electron volts is calculated by means of Wall's equation $E_\infty = 3NkT$, where E_∞ is the equilibrium modulus, N the number of crosslinks per 100 electron volts, T the absolute temperature and k the Boltzman constant, then to the first approximation a linear relationship is found between the number of crosslinks and the vinylidene fluoride content of the copolymer (Fig. 7).

These results give grounds for the assumption that on irradiation of rubber-like, fluorine-containing copolymers practically the same reactions occur as in the irradiation of polyethylene, namely, the C—H bond is ruptured with the formation of a polymeric radical and a hydrogen atom, the hydrogen atom can abstract a hydrogen, fluorine or chlorine atom from another polymer chain with the formation of a second polymeric radical and a molecule of H_2, HF and HCl. Recombination of these radicals leads to crosslinking of the chains. In addition the hydrogen atom can abstract an H, F or Cl atom from a neighbouring carbon atom with the formation of double bonds of the type $-CF=CF-$ or $-CF=CH-$.

$$-CF_2-CFCl-CF_2-CH_2- \rightarrow H^{\cdot} + -CF_2-CFCl-CF_2-CH^{\cdot} \longrightarrow$$

$$\rightarrow -CF_2-CFCl-CF=CH- + HF.$$

$$-CF_2-CFCl-CH_2-CF_2- \rightarrow H^{\cdot} + -CF_2-CFCl-CH^{\cdot}-CF_2 \rightarrow$$

$$\rightarrow -CF_2-CF=CH-CF_2- + HCl.$$

The presence in the spectrum of the irradiated copolymer of bands in the 1640 and 1740 cm^{-1} regions, corresponding to $-CF=CH-$ and $-CF=CF-$ double bonds confirms this reaction course, and it is also possible that the first type of bond could be formed by the splitting off of fluorine atoms from two neighbouring carbon atoms in the chain with the formation of a molecule of F_2. The decrease in the intensity of the bands corresponding to the C—H, C—Cl and C—F bonds in the spectrum of the irradiated polymer confirms that these bonds are ruptured during irradiation.

Investigation of the viscosity of solutions of the uncrosslinked portion of the copolymer after irradiation showed that degradation occurs alongside crosslinking, because the reduced viscosity of the soluble portion of the irradiated copolymer falls considerably with increase in radiation dosage (Fig. 8).

The absorption bands in the spectrum of the irradiated copolymer corresponding to the terminal double bonds, $-CF=CF_2$ (1800 cm^{-1}) and $-CH-CF_2$ (1740 cm^{-1}), also indicate the occurence of degradation processes. These groups probably arise as a result of disproportionation between polymeric radicals, $RCF_2-CF_2^{\cdot} + {}^{\cdot}CF_2-CF_2-R' \rightarrow RCF_2-CF_3 + CF_2=CFR'$ or of depolymerization of radicals, $RCF_2-\dot{C}FR' \rightarrow \dot{R} + CF_2=CFR'$.

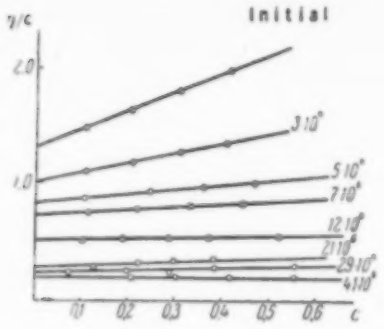

FIG. 8. Change in reduced viscosity of the solution of uncrosslinked copolymer during irradiation of the fluoro-rubber.

CONCLUSIONS

Investigation of the infrared spectra of rubber-like, fluorine-containing copolymers has shown that when these copolymers are irradiated with γ-rays from a ^{60}Co source double bonds are formed. On irradiation in air, in addition to double bonds, oxygen-containing and hydroxyl groups are formed by oxidation and reaction with water vapour from the air. At the same time there is a decrease in strength of the absorption bands corresponding to the stretching frequencies of the C—H, C—F and C—Cl bonds, indicating the evolution of volatile products during irradiation.

An increase in the hydrogen content of the copolymer leads to an increased concentration of double bonds on irradiation.

During irradiation, in addition to crosslinking of the fluorine-containing copolymer degradation is observed, as indicated by a decrease in the reduced viscosity of the uncrosslinked copolymer.

Translated by E. O. PHILLIPS

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INVESTIGATIONS IN THE FIELD OF CO-ORDINATION-CHAIN POLYMERS—II. SOME POLYMERS OF QUINIZARIN WITH METALS*

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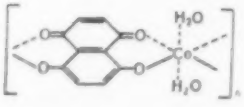
IN a previous communication one of us with his collaborators [1] described the production of polymers with internal complex linkages based on various bis-(β-diketones) and metals.

As ligands for the preparation of linear, co-ordination polymers, in addition to tetraketones other organic compounds containing four atoms capable of forming ring structures with metals of co-ordination number four, may also be used. We were interested in examining the possibility of forming co-ordination polymers from 1,4-dihydroxyanthraquinone (quinizarin). Bailes and Calvin [2] showed in 1947 that naphthazarin could form, with cobalt salts, polymers of the structure



Quinizarin has a similar structure to naphthazarin, the only difference being that its molecule contains one more aromatic nucleus. In view of this it would be thought that quinizarin should also form polymers with metal salts. In 1939 and 1942 Flumiani and Bajić [3] described the preparation of copper salts of hydroxyanthraquinone, of various structures. In particular, on treating a boiling, alcoholic solution of quinizarin with aqueous copper sulphate solution in the presence of a few drops of sulphuric acid they obtained a copper salt of quinizarin of the composition, $C_{14}H_6O_2(O)_{1\cdot4}CH_2(O)_{1\cdot4}O_2C_{14}H_6$, which in our opinion must be a co-ordination polymer of quinizarin and copper but it was not regarded from this point of view by Flumiani and Bajić.

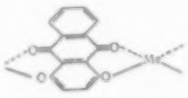
When this communication was in the press a paper by Knobloch and Rauscher appeared, on the preparation of co-ordination polymers of copper at an interfacial boundary. In particular they were able to obtain a polymer of copper and quinizarin, containing 20·6 per cent of copper, by reacting a benzene solution of quinizarin with an aequeous solution containing the copper-ammonium complex ion [4].

* Vysokomol. soedin. **2**: No. 4, 492–497, 1960.

The present paper describes the preparation of co-ordination polymers of quinizarin with zinc, manganese, cobalt, nickel, copper and cadmium.

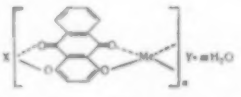
DISCUSSION

Data on the co-ordination compounds of quinizarin obtained are given in Tables 1 and 2. By analogy with the coordination polymers of naphthazarin it would be expected that in the case of quinizarin the structure of the repeating unit of the polymer would be the following:



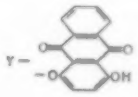
The end groups of such a polymer could be either a quinizarin or an acetylacetone group (or an acetate group if instead of a metal acetylacetonate an acetate of the metal is used as the metal derivative for the reaction), or one quinizarin and one acetylacetone groups (or an acetate group) simultaneously. It is possible also that the polymer could contain water of crystallization in view of the presence of metal atoms in the polymer chain.

By comparing the elementary composition found for the products from the reaction between quinizarin and the metal derivatives with that calculated for the compound



(where X is H or $MeCH(COCH_3)_2$ (or $MeOOCCH_3$), or $Me[CH(COCH_3)_2]_2$ (or $Me(OOCCH_3)_2$);

Y is



or $CH(COCH_3)_2$ (or $-OOCCH_3$) or$[CH(COCH_3)_2]_2$ (or $(OOCCH_3)_2$, n is any whole number (when n is large X and Y can be neglected), m is zero or any number. We were able in the majority of cases to establish the formulae of the quinizarin co-ordination polymers (see Table 1). Table 1 shows that a low degree of polymerization is characteristic of most of the polymers with the exception of those based on manganese. For example zinc gives a hexamer, copper a pentamer and nickel a dimer and a decamer. A rather higher degree of polymerization (11–20) was obtained in the case of the cobalt polymer. It can be seen from the example of the co-ordination compounds of nickel that it is possible to vary the molecular weight of the polymer by varying the preparative conditions. Thus by carrying out the reaction in solution in dinil* with an excess of nickel

* *Translator's note*: A Russian commercial name—*Editor*.

TABLE 1. CO-ORDINATION POLYMERS OF QUINIZARIN WITH VARIOUS METALS

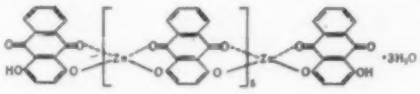
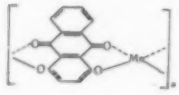
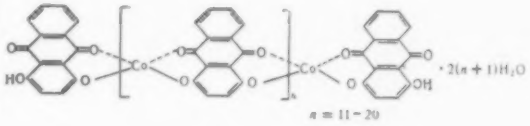
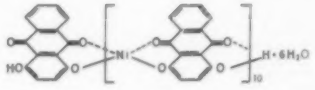
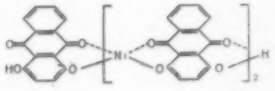
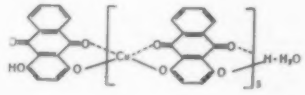
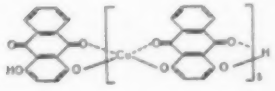
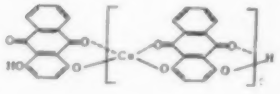
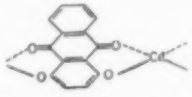
No.	Elementary composition (%)						Formula
	Found			Calculated			
	C	H	Me	C	H	Me	
1	55·48	2·43	18·27	55·62	2·36	18·56	
	55·48	2·55	18·22				
2	57·00	2·63	18·73	57·35	2·05	18·40	
	57·24	2·58	18·84		$n = 11$		
3	51·61	3·31	17·16	51·67	3·02	16·16	
	51·73	3·21	17·12	51·15	3·02	17·09	
					$n = 20$		
4	55·71	2·52	17·37	55·75	2·41	17·70	
5	60·14	2·40	13·76	60·49	2·39	14·08	
	60·20	2·61	13·59				
6	57·06	2·55	17·96	57·09	2·26	17·98	
	56·94	2·74	17·89	57·74	2·18	18·19	
				57·45	2·15	18·61	
7	38·53	2·50	36·05	47·94	1·71	32·07	
	38·40	2·40	36·09				

TABLE 2. CO-ORDINATION POLYMERS OF QUINIZARIN WITH VARIOUS METALS

No.	Metal	Behaviour on heating in a capillary tube	Temperature of greatest change in dimensions of the sample (°C[2])	Solubility of polymer in cresol	Crystallinity of sample	Molecular weight[3]
1	Zinc	Begins to decompose at 340°	396	2·59	Crystalline, with very poor order within the crystal	2110
2	Manganese	Unchanged up to 480°	368	0·73	Crystalline, with crystals of large dimensions	—
3	Cobalt	,,	318	1·11	Amorphous	3900–6900
4	Nickel	,,	>400	—	Crystalline	3320
5	,,	Begins to decompose at 270°	406	0·51	As No. 2	836
6	Copper	Begins to decompose at 270°	332	0·91	,, ,, ,,	1000
7	Cadmium	Unchanged up to 480°	350	0·35	Crystalline, with very poor order within the crystal	—

acetylacetonate the degree of polymerization can be increased by a factor of 5. Obviously an increase in the molecular weight of the polymers of other metals is also possible.

The fact that some of the quinizarin co-ordination polymers contain water of crystallization was shown by further drying of the polymer to constant weight, determining the metal content of the dried polymer and comparing the change in metal content with the loss in weight, which we consider to result from the loss of water of crystallization. For example, the co-ordination polymer of quinizarin with zinc on drying for 6 days at 180–200°C lost weight by 2·2 per cent. The zinc content found after drying was 18·88; 19·09 per cent, which is in good agreement with the value for zinc (19·05 per cent) calculated on the assumption that the loss in weight of the polymer results from loss of water of crystallization.

It is seen from Table 2 that all the quinizarin co-ordination polymers are black powders which, however, would be expected from the accumulation in the molecule of systems with conjugated double bonds. These quinizarin co-ordination compounds are of characteristically low solubility. They are completely insoluble in such organic solvents as alcohol and chloroform. They are very insoluble in dinil and dimethylformamide, though they colour these solvents

a little. The zinc co-ordination compound has the highest solubility in cresol but here the solubility is only 2·6g/l.

On heating the quinizarin co-ordination polymers of manganese, cobalt, nickel (decamer) and cadmium in a capillary tube no change in external appearance was observed and no volatile products were evolved up to 480°C. On heating the zinc, nickel (dimer) and copper polymers in a capillary tube, beginning at 340, 275 and 300° respectively, decomposition of the polymer was observed with the appearance of an orange substance in the sublimate (found to be quinizarin) in the first two cases, and in the third case a violet-coloured substance.

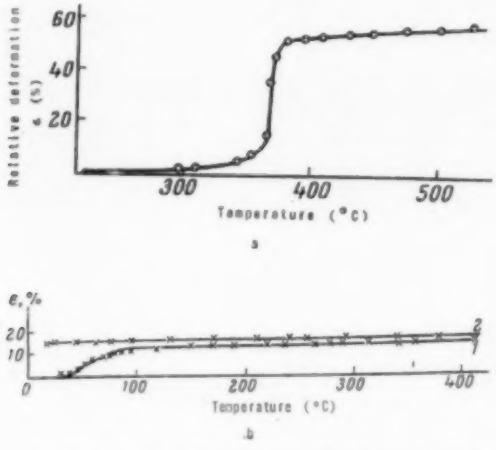


FIG. 1. Thermomechanical curves of polymers of quinizarin: (a) with manganese; (b) with nickel (decamer): (1) initial, (2) heated to 400°C.

Thermomechanical curves of the quinizarin co-ordination polymers showed that the greatest change in the dimensions of the polymers takes place at the following temperatures: for the zinc polymer, ~396°; for the manganese polymer, ~368°; for the cobalt polymer, ~318°; for the copper polymer, ~332°; for the nickel polymer, above 400°; for the cadmium polymer ~350°.

Evidently, with the exception of the nickel polymer, these figures denote the temperature at which fairly vigorous decomposition of the polymers occurs. As an example Fig. 1a shows the thermomechanical curve of the polymer of quinizarin with manganese. On the basis of this it may be assumed that the polymer decomposes mainly in the region ~300–380° (where the change in dimensions of the sample is greatest). The polymer evidently decomposes completely by ~380° because a subsequent rise in temperature up to 500° causes no further change in its dimensions. Figure 1b shows thermomechanical curves of the quinizarin co-ordination polymer with nickel (decamer). Curve 2 was plotted for a sample that had previously been used for plotting a thermomechanical curve (curve 1), i.e. it had previously been heated to 400°. It may be

concluded from these curves that this polymer does not decompose or soften below 400°. The deformation that occurs in the temperature region up to ~100° is evidently caused by loss of water of crystallization.

On the basis of the above data it may be concluded that the heat stability of the co-ordination polymers of quinizarin with this series of metals decreases in the following order:

$$Ni > Zn > Mn > Cd > Cu > Co .$$

An X-ray diffraction examination of the polymers showed that the polymer containing cobalt is an amorphous material; the polymer with nickel (decamer) is crystalline; those with zinc and cadmium have an essentially crystalline structure with poor order within the crystal, and those with manganese, nickel

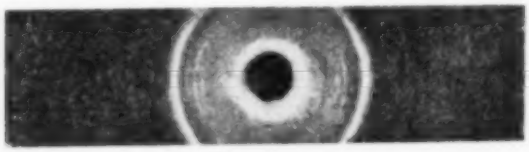


FIG. 2. X-ray diffraction pattern of the co-ordination polymer of quinizarin with nickel (decamer).

(dimer) and copper are crystalline with the crystals of large dimensions. On Figure 2 the X-ray diffraction pattern of the quinizarin co-ordination polymer with nickel (decamer) is shown as an example.

EXPERIMENTAL

The synthesis of quinizarin co-ordination polymers. The preparation of the quinizarin co-ordination polymers described in this paper was carried out by two methods:

(1) By heating equimolecular mixtures of quinizarin and the acetylacetonate of the metal in a condensation tube, first in a current of nitrogen at 100–220° for 1 hour, then 220° for 1 hour and then *in vacuo* at ~2mm for 1 hour at 220°. After heating, the polymer was treated with boiling *p*-xylene and ethanol to remove unreacted starting materials and was then washed with ether and dried. The zinc, copper and nickel polymers were prepared by this method and are denoted as Nos. 1, 5 and 6 in Tables 1 and 2;

(2) The reaction was carried out in a current of nitrogen or in dimethylformamide (polymers No. 2, 3 and 7 in Tables 1 and 2) at 120–140° for 4–6hr, or in dinil (polymer No. 5 in Tables 1 and 2) at 120–140° for 6hr. After heating, the polymers were treated in a manner similar to that of the first method. In the case of the polymers of quinizarin with manganese, cadmium and cobalt an excess of quinizarin over the metal acetates was used and in the case of the nickel polymer (polymer No. 5) the acetylacetonate of the metal was taken in excess.

The authors express gratitude to workers in the laboratories under the leadership of G. L. Slonimskii and A. I. Kitaigorodskii for carrying out the thermomechanical and X-ray diffraction examination of the polymers.

CONCLUSIONS

Polymetallic derivatives based on quinizarin and the following metals: zinc, copper, manganese, nickel, cobalt and cadmium, have been synthesized and investigated.

Translated by E. O. PHILLIPS

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INVESTIGATIONS IN THE FIELD OF CO-ORDINATION POLYMERS—III. CO-ORDINATION POLYMERS BASED ON bis-(8-HYDROXYQUINOLYL) METHANE*

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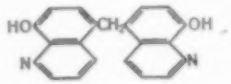
(*Received* 17 *December* 1959)

IN the previous paper in this series [1] data were presented on some polymers of quinizarin with metals. The purpose of this work was to synthesize and examine co-ordination polymers of bis-(8-hydroxyquinolyl)methane alone, and mixed co-ordination polymers based on bis-(8-hydroxyquinolyl)methane and quinizarin.

It is known from the literature that 8-hydroxyquinoline is a good complexing agent, finding wide application in the separation and determination of various metals [2]. 8-hydroxyquinoline itself cannot be used for the preparation of co-ordination polymers because it is a bidentate compound. In order to obtain co-ordination polymers with metals of co-ordination number four the ligand must be tetradentate. Such a tetradentate compound is the derivative of 8-hydroxyquinoline, bis-(8-hydroxyquinolyl)methane:



The presence in this of two complex-forming groups

that are well separated from one another suggests that co-ordination polymers could be formed with this ligand.

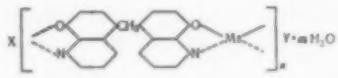
In this communication the preparation is described of such polymers of bis-(8-hydroxyquinolyl)methane with zinc, manganese, cobalt, nickel, copper and cadmium.

In addition to the preparation of co-ordination polymers based on bis-(8-hydroxyquinolyl)methane alone we also attempted to prepare some mixed polymers based on this ligand and quinizarin, with the same metals.

* Vysokomol. soedin. **2**: No. 4, 498–507, 1960.

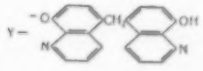
DISCUSSION

The data obtained on the co-ordination polymers of bis-(8-hydroxyquinolyl) methane are given in Tables 1 and 2. The following formula represents the suggested general form of these polymers:



where X is H or MeCH $(COCH_3)_2$ (or $MeOOCCH_3$) or $Me[CH(COCH_3)_2]_2$ (or $Me(OOCCH_3)_2$).

Y is



or $-CH(COCH_3)_2$ (or $-OOCCH_3$) or $[CH(COCH_3)_2]_2$ (or $(OOCCH_3)_2$), n is any whole number, at high values of which X and Y can be neglected, and m is zero or any number.

Comparison of the elementary composition found for these co-ordination polymers with that calculated for the above formula enabled a number of suggestions to be made on the structure of the products obtained.

When it is considered that in the actual polymer, at sufficiently large values of n, it is often possible to have a combination of polymers with the various types of end groups, it may be considered that the found and calculated elementary compositions given in Table 1 are in fair agreement with one another.

It follows from Table 1 that polymeric co-ordination compounds are formed by the interaction of bis-(8-hydroxyquinolyl)methane with metallic derivatives in the majority of cases. Only in the case of copper and nickel were low-molecular compounds obtained—the trimer and dimer respectively.

It can be seen from Table 2 that such properties of the co-ordination polymers as colour, heat stability and crystallinity depend on the nature of the metal with which the polymer was prepared. For example, the polymer containing zinc has a yellow colour with a reddish tone, that containing nickel a light brown colour and the polymer containing cadmium is yellow-green. The polymers containing cobalt have a characteristic greenish colour with a brown tone, those with manganese a dull green and those with copper a yellow-green colour. Some of the bis-(8-hydroxyquinolyl)methane co-ordination polymers change colour on heating in a capillary tube. This is evidently the result of decomposition. For the polymer containing zinc this occurs at 270–280°C, for the cadmium polymer at 320° and for the manganese polymer at 290°.

Comparison of these decomposition temperatures of the polymers with the shape of their thermomechanical curves shows that the change in dimensions of the polymers with increase in temperature is not a consequence of softening but results from their thermal decomposition. As an example to illustrate this

the thermomechanical curve of the polymer containing zinc (No. 1 in Tables 1 and 2) is shown in Fig. 1. On comparing its shape with the temperature at which decomposition begins (270–280°), as observed in the capillary tube, it can be observed that the deformation of the polymer in the temperature region of 280–370° is brought about by its decomposition, the rate of which is greatest in the region of 370°. The fact that the polymer has already completely decomposed by about 380° is confirmed by the shape of the thermomechanical curve at higher temperatures which indicates no further change in the dimensions of the polymer. The figures in column 4 of Table 2 show the temperatures (from the thermomechanical curves) at which thermal decomposition of the polymers evidently takes place. The first figure indicates the temperature at which decomposition begins, the second gives the nominal temperature at which decomposition proceeds at a significant rate (it is obtained as the point of intersection of the slopes of the thermomechanical curve). It follows from Table 2 that the bis-(8-hydroxyquinolyl)methane co-ordination polymers are heat stable within the temperature range 250–320° (according to the initial decomposition temperature).

FIG. 1. Thermomechanical curve of the polymer of bis-(8-hydroxyquinolyl)methane with zinc.

An X-ray diffraction study of these polymers showed that the majority of them are crystalline. Figure 2 shows, as examples, the X-ray diffraction patterns of the polymers with zinc and cadmium.

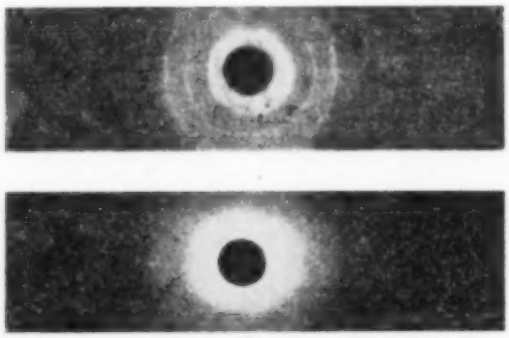


FIG 2.

The bis-(8-hydroxyquinolyl)methane polymers are insoluble in such solvents as water, ethanol, methanol, ether, petroleum ether, benzene, toluene, xylene, cresol, nitrobenzene, pyridine, chloroform, carbon tetrachloride, dilute acetic

acid, dilute sulphuric acid, and alkali. The polymers dissolved in glacial acetic acid, formic acid and concentrated sulphuric acid but in the latter decomposition of the polymer obviously occurs.

In addition to the preparation of co-ordination homopolymers we attempted to prepare mixed co-ordination polymers. Thus polymers based on bis-(8-hydroxyquinolyl)methane and two metals were prepared and also from bis-(8-hydroxyquinolyl)methane and quinizarin with some of the metals.

The data obtained on these polymers is presented in Tables 3 and 4. All the products are coloured, infusible powders, soluble like the bis-(8-hydroxyquinolyl)methane polymers, only in glacial acetic, formic and concentrated sulphuric acids.

All the products given in Table 3 have characteristic, uniform colours, different from those of the corresponding homopolymers. For example the homopolymer of bis-(8-hydroxyquinolyl)methane with nickel is light brown, the corresponding quinizarin polymer is black in colour and the product obtained from bis-(8-hydroxyquinolyl)methane, quinizarin and nickel acetylacetonate is greyish-black. The co-ordination homopolymer of bis-(8-hydroxyquinolyl)-methane with manganese is dull green in colour and the corresponding quinizarin polymer is black whereas the product from the simultaneous reaction of bis-(8-hydroxyquinolyl)methane and quinizarin with manganese acetylacetonate has a characteristic black colour with a pronounced blue tint, etc.

Comparison of the found elementary composition of the polymers, shown in Table 3, with their different possible structures enables the ratios of the component parts of some of the copolymers to be found. Thus the ratio of the component parts [bis-(8-hydroxyquinolyl)methane unit: zinc: copper] in the mixed polymer obtained from bis-(8-hydroxyquinolyl)methane with copper and zinc acetylacetonates (No. 1, Tables 3 and 4), is 2:1:1. One of the possible structural variants of a copolymer with these ratios is shown in column 5 of Table 3.

The ratio of the component parts [bis-(8-hydroxyquinolyl)metane unit:quinizarin unit:cobalt] in the mixed polymer from bis-(8-hydroxyquinolyl)methane, quinizarin and cobalt acetate when the initial reactants were taken in the ratios 0·5:0·5:1 respectively, was 2:1:3 (No. 6, Tables 3 and 4). The high content of bis-(8-hydroxyquinolyl)methane in the mixed polymer indicates its greater reactivity as a ligand with cobalt acetate in comparison with quinizarin. This is seen particularly clearly when an excess of cobalt acetate is used (No. 7, Tables 3 and 4). In this case the content of the less reactive quinizarin in the polymer falls to only one unit to four bis-(8-hydroxyquinolyl)methane units.

EXPERIMENTAL

bis-(8-hydroxyquinolyl)methane. bis-(8-hydroxyquinolyl)methane sulphate was synthesized according to Shüller [3] by reacting 8-hydroxyquinoline with formaldehyde in concentrated sulphuric acid at 0−+5°. bis-(8-hydroxyquinolyl)-methane was obtained from the sulphate by decomposing the salt in aqueous ammonia. The yield of bis-(8-hydroxyquinolyl)methane was 52 per cent of theory

TABLE 1. CO-ORDINATION POLYMERS OF

No.	Metal	Elementary composition (%)							
		Found				Calculated			
		C	H	N	Me	C	H	N	Me
1	Zinc	58·40 58·49	3·55 3·49	6·98 6·95	17·92 18·00	58·10	3·82	7·12	16·66
2	,,	61·79	3·54	8·07	16·58	60·90	3·20	7·49	17·47
		61·81	3·62	8·14	16·60	61·41	3·35	7·46	16·80
3	Nickel	64·10 64·34	3·88 3·76	7·33 7·29	12·00 12·2	63·72	4·19	7·82	10·93
4	,,	67·01 67·04	4·00 3·74	8·57 8·51	9·55 9·50	67·18	3·97	7·94	8·65
5	Cadmium	54·63	3·36	7·56	26·41	54·10	3·08	6·64	26·67
		54·43	3·43	7·59	26·30	55·10	2·97	6·70	26·70
6	Cobalt	57·19 57·47	3·89 3·95	7·34 7·23	14·43 14·60	57·72	3·28	7·09	14·92
7	Manganese	62·72 62·70	3·67 3·65	8·13 7·19	15·81 15·79	62·63	3·57	7·68	15·08
8	Copper	63·77 63·95	3·75 3·17	7·88 8·07	14·54 14·68	64·21	3·31	7·88	14·13

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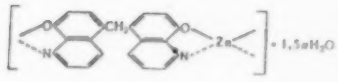
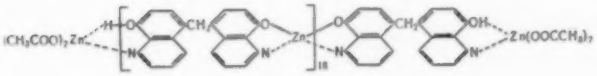
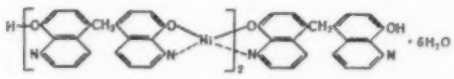
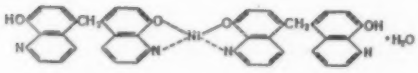
BIS-(8-HYDROXYQUINOLYL) METHANE WITH VARIOUS METALS

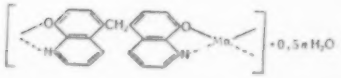
Formula of polymer

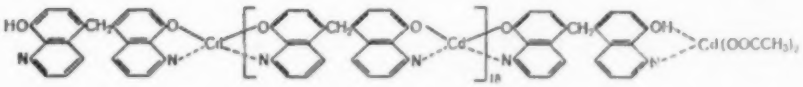


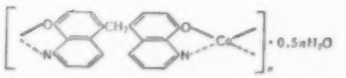












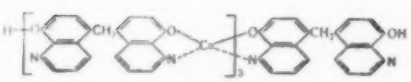


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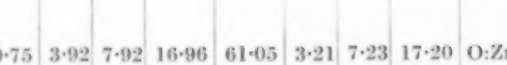
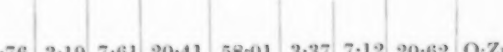
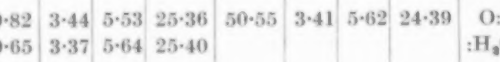
TABLE 2. CO-ORDINATION POLYMERS OF BIS-(8-HYDROXYQUINOLYL) METHANE WITH VARIOUS METALS

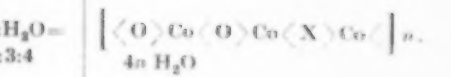
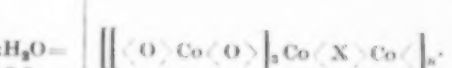
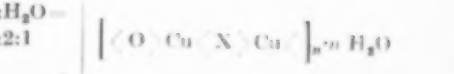
No.	Metal	Behaviour on heating in a capillary tube*	Temperature range of change in dimensions (from the thermomechanical curve) (°C)	Data from the X-ray diffraction study of the sample	Molecular weight from elementary analysis	Colour of polymer
1	Zinc	Darkens at 270°	280–370	Crystallinity, unusual for large molecules of complex structure	—	Yellow with reddish tone
2	„	Darkens at 270–280°	200–450	„	7240	„
3	Nickel	—	240–380	Chain molecule order. It may be considered that the metal atoms from a true lattice	—	Light brown
4	„	—	320–380	Crystallinity, unusual for large molecules of complex structure	680	„ „
5	Cadium	Darkens at 320°	280–380	Chain molecule order. It may be considered that the metal atoms form a true lattice	8370	Yellow-green
6	Cobalt	—	250–400	Very weak X-ray diffraction of gaseous type	—	Greenish with brown
7	Manganese	Darkens at 290°	260–350	As for polymer No. 5	—	Dull green
8	Copper	—	320–360	—	1390	Yellow-green (darker than No. 5)

* No melting was observed in any sample up to 400°

TABLE 3. MIXED CO-ORDINATION POLYMERS

No	Starting materials and ratios	Elementary composition (%)								Ratio of components in polymer	One of the possible structural variants
		Found				Calculated					
		C	H	N	Me	C	H	N	Me		
1	bis-(8-hydroxyquinolyl) methane: :$[(CH_3CO)_2CH]_2Zn$: :$[(CH_3CO)_2CH]_2Cu$= =1:0·5:0·5	60·75 60·52	3·92 3·73	7·92	16·96	61·05	3·21	7·23	17·20	O:Zn:Cu:H_2O= =2:1:1:1	
2	bis-(8-hydroxyquinolyl) methane: :$(CH_3COO)_2Zn$: :$(CH_3COO)_2Cd$= =1:0·5:0·5	58·76 58·50	3·19 3·14	7·61 7·47	20·41 20·59	58·01	3·37	7·12	20·62	O:Zn:Cd:H_2O= =3:2:1:2	
3	bis-(8-hydroxyquinolyl) methane: :$(CH_3COO)_2Zn$: :$(CH_3COO)_2Cd$= 1:1:1	49·82 49·65	3·44 3·37	5·53 5·64	25·36 25·40	50·55	3·41	5·62	24·39	O:Zn:Cd:Yk: :H_2O=2:2:1:2:2	
4	bis-(8-hydroxyquinolyl) methane:quinizarin: :$(CH_3COO)_2Ni$= =0·5:0·5:1	57·22 57·15	4·70 4·61	5·30 5·39	13·05	57·95	3·90	5·70	13·97	O:X:Ni:H_2O= =3:1:4:4	

(continuation of the Table 3 from the page 351)

No.	Starting materials and ratios	Elementary composition (%)								Ratio of components in polymer	One of the possible structural variants
		Found				Calculated					
		C	H	N	Me	C	H	N	Me		
5	bis-(8-hydroxyquinolyl) methane:quinizarin: :$(CH_3COO)_2Zn$ = 0·5:0·5:1	52·19 52·32	3·85 3·69	5·84 5·73	20·49 20·43		—			—	—
6	bis-(8-hydroxyquinolyl) methane:quinizarin: :$(CH_3COO)_2Co$ = 0·5:0·5:1	57·03 57·30	3·32 3·44	4·90 4·93	16·55 16·40	57·41	3·58	5·16	16·27	O:X:Co:H_2O = = 2:1:3:4	 n, $4n\ H_2O$
7	bis-(8-hydroxyquinolyl) methane:quinizarin: :$(CH_3COO)_2Co$ = 1:1:1	59·61 59·79	3·77 3·69	7·07 7·09	14·95 14·70	59·80	3·51	6·14	14·52	O:X:Co:H_2O = = 4:1:5:5	 $\cdot 5n H_2O$
8	bis-(8-hydroxyquinolyl) methane:quinizarin: :$(CH_3COO)_2Mn$ = 0·5:0·5:1	51·11	3·13	5·19	18·70		—			—	—
9	bis-(8-hydroxyquinolyl) methane:quinizarin: :$(CH_3COO)_2Cu$ = 0·5:0·5:1	57·66	3·08	4·72	18·94	58·01	2·77	4·09	18·57	O:X:Cu:H_2O = = 1:1:2:1	 $\cdot n\ H_2O$

O is bis-(8-hydroxyquinolyl)methane;
X is quinizarin; Ac is CH_3COO-.

TABLE 4. MIXED CO-ORDINATION POLYMERS

No.	Starting materials and ratios (moles)	Behaviour on heating in a capillary *	Temperature range of change of dimensions of sample (from the thermomechanical curves) (°C)	Colour of polymer
1	bis-(8-hydroxyquinolyl)methane:$(CH_3CO)_2CH_2Cu$ = 1:0·5:0·5	Darkens at 270°	260–350	Green with yellow tone
2	bis-(8-hydroxyquinolyl)methane:$(CH_3COO)_2Zn$:$(CH_3COO)_2Cd$ = = 1:0·5:0·5	Darkens at 320°	320–398	Lemon-yellow
3	bis-(8-hydroxyquinolyl)methane:$(CH_3COO)_2Zn$:$(CH_3COO)_2Cd$ = 1:1:1	Darkens at 260°	200–390	Rather lighter than the preceding
4	bis-(8-hydroxyquinolyl)methane:quinizarin:$(CH_3COO)_2Ni$ = 0·5:0·5:1	—	—	Greyish-black
5	bis-(8-hydroxyquinolyl)methane:quinizarin:$(CH_3COO)_2Zn$ = 0·5:0·5:1	—	220–330	Light-orange-brown
6	bis-(8-hydroxyquinolyl)methane:quinizarin:$(CH_3COO)_2Co$ = 0·5:0·5:1	—	—	Black
7	bis-(8-hydroxyquinolyl)methane:quinizarin:$(CH_3COO)_2Co$ = 1:1:1	—	—	Black with green tone
8	bis-(8-hydroxyquinolyl)methane:quinizarin:$(CH_3COO)_2Mn$ = 0·5:0·5:1	—	220–360	Black with blue tone
9	bis-(8-hydroxyquinolyl)methane:quinizarin:$(CH_3COO)_2Cu$ = 0·5:0·5:1	—	220–350	Dark brown with tobacco tone

* No melting was observed up to 400° in all samples.

and its decomposition temperature was 246°. The product was purified by four-fold recrystallization from dimethylformamide.

	Found %:	C 75·50, 75·30;	H 4·85, 5·06; N 9·41, 9·26
$C_{19}H_{14}N_2O_2$	Calculated %:	C 75·48;	H 4·63; N 9·27.

Preparation of the co-ordination polymers. The co-ordination polymers described in this communication were prepared by two methods:

(1) By heating an equimolecular mixture of the ligand and the acetylacetonate of the metal in a condensation tube, first in a current of nitrogen at 100–220° (1 hr), at 220° for 1 hr and then *in vacuo* (1–2 mm) at 220° for 1 hr. After heating the polymer was freed from starting materials by consecutive treatment with boiling nitrobenzene and alcohol, and was then washed with ether and dried. The polymer of bis-(8-hydroxyquinolyl)methane with zync, denoted as No. 1 in Tables 1 and 2, was prepared by this method.

(2) The reaction was carried out in a current of nitrogen in dimethylformamide (polymers No. 2 and 4–8 in Tables 1 and 2, and No. 1–9 in Tables 3 and 4) at 120–140° for 4–6 hr, or in dinil (polymer No. 3 in Tables 1 and 2) at 230° for 3 hr. At the end of the reaction the hot solution was filtered and the residue was treated with boiling water and alcohol, washed with ether and dried. In the case of the co-ordination homopolymers the reactants were taken in equimolecular proportions.

In conclusion the authors express gratitude to workers in the laboratories under the leadership of G. L. Slonimskii and A. I. Kitaigorodskii for carrying out the mechanical and X-ray diffraction examinations of the polymers.

CONCLUSIONS

(1) Co-ordination homopolymers of bis-(8-hydroxyquinolyl)methane with zinc, copper, manganese, nickel, cadmium and cobalt have been prepared and investigated.

(2) The following mixed co-ordination polymers have been prepared: bis-(8-hydroxyquinolyl)methane with zinc and copper, bis-(8-hydroxyquinolyl)-methane with zinc and cadmium; bis-(8-hydroxyquinolyl)methane and quinizarin with nickel and with zinc, cobalt, manganese and copper respectively.

(3) On the example of mixed co-ordination polymers of bis-(8-hydroxyquinolyl)methane and quinizarin it has been shown that the former has a higher complex-forming activity than quinizarin.

Translated by E. O. PHILLIPS

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THE ROLE OF SURFACE ELECTRON DEFECTS IN HETEROGENEOUS CATALYTIC POLYMERIZATION—I. ALFIN-TYPE POLYMERIZATION*

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THE processes of heterogeneous catalytic polymerization have recently acquired practical and scientific importance. However the mechanism of the catalysis still remains obscure.

The aim of the present work is an attempt to interpret the mechanism of polymerization in the presence of heterogeneous catalyst. In this first communication the Alfin system [1, 2] (a combination of an alkyl chloride, a secondary alcohol, an alkali metal and an olefine)] is examined as an example. In addition to their high activity Alfin catalysts are capable of giving crystalline polymers under certain conditions. It is known also [3] that the alkali metal halide is an essential component of the catalyst as well as the alcoholate (e.g. the isopropylate) and the metal derivative of the olefine (e.g. allylsodium). For example, with either NaCl or $NaOCH(CH_3)_2$ alone in the presence of allylsodium the yield of polymer is ~ 4 per cent, whereas when they are both present the yield is ~ 65 per cent.

Morton suggests [3, 4] that the basis of the catalyst is a co-ordination complex containing $Na^+(CH_2{=}CHCH_2)^-$, $Na^+OR'^-$ and Na^+Cl^-. Polymerization is initiated as a result of adsorption of the monomer, for example butadiene, isoprene or styrene, on to two points on the surface of this complex:

$$CH_2{=}CHCH_2^-Na^+\dot{C}_4H_6 \longrightarrow CH_2{=}CHCH_2 + \dot{N}aC_4H_6\,,$$

$$\dot{N}aC_4H_6 \longrightarrow Na^+\bar{C}H_2{-}CH{=}CH{-}\dot{C}H_2$$

and then rapid polymerization occurs:

$$Na^+\bar{C}H_2CH{=}CH\dot{C}H_2 + nC_4H_6 \longrightarrow Na^+\bar{C}H_2CH{=}CHCH_2\,(C_4H_6)_n$$

Uelzman [5], however, discusses an anionic mechanism in which the complex Na^+Cl^- $(\leftarrow Na^+R^-)Na^+OR^-$ and polarized molecules, $CH_2{=}CHCH^+{-}\bar{C}H_2$, take part. Curphey [6] also proposes an anionic mechanism based on electromeric changes in the monomer connected with the chemical structure of the catalyst components.

* Vysokomol. soedin. **2**: No. 4, 529–534, 1960.

Such types of mechanism do not reflect the nature of the alkali metal halide, the role of the secondary alcoholate, the nature of the monomer etc. This indicates a need to seek new possibilities for explaining the numerous experimental data in this field.

It is known [7] that many effective heterogeneous catalysts are coloured. Roginskii [7] has already drawn attention to the correlation between the colour of the catalyst and its catalytic activity, in connection with the possibility of electron transferences. We suggest that electron defects of the "colour centre" type, that have characteristics electron donor properties, play an essential part in the mechanism of heterogeneous catalysis. Coloured alkali metal halide crystals [8–12] are model systems of this type. Alkali metal halides under certain circumstances [8, 9] acquire various colours. The physical process, for example of additive coloration, leads to the introduction of a stoichiometric excess of the metal into the lattice which is ionized in the field of the lattice. Then in virtue of the electronegativity of the crystal as a whole anionic vacancies are "formed", about which the free electrons that arise are localized. Such defects with electrons surrounding them are called *F*-centres or "colour centres". In addition to these, other, more complex, centres can also be formed, for example $F'-$, F_2-, F_2^+-, *U*-centres etc. [8, 9, 12] that can obviously take part in the chemisorption process in question. The coloration is attributed to excitation of the electrons in the *F*-centre. These views on the nature of *F*-centres are confirmed by absorption spectra, electron paramagnetic resonance spectra and other physical measurements [11].

In view of the above considerations we suggest that electron defects of the "colour centre" type that readily form under the conditions of preparation of heterogeneous polymerization catalysts (and of other processes), take an essential part in the activation of saturated and unsaturated molecules for addition reactions. In particular it may be considered that the necessary weakening of the π-bonds in the monomer takes place as a result of dative interaction in which the unoccupied anti-bonding molecular orbital of the bond undergoing activation and the approaching molecular orbital of the active centre of the catalyst, where there is an unpaired electron, take part. It is the inclusion of the anti-bonding molecular orbital in the general bonding that brings about the necessary activation with respect to addition reactions. To illustrate this point of view some experimental data and some views on chemisorption on metals may be quoted

When molecular hydrogen is adsorbed on to "pure" metals it dissociates [13]. Evidently in this case, other conditions being equal, some sharing of an electron localized near one or other defect, or possibly of electrons of the transfer zone, takes place with the anti-bonding orbital of the hydrogen molecule. We consider that in addition to dative interaction, essential for the activation of chemisorbed molecules with respect to addition reactions, "ordinary" interaction between electron pairs on the combining H orbitals with a suitable vacant orbital of the defect, is also possible. In the adsorption of ethylene on nickel on which

some hydrogen has already been adsorbed, the C_2H_4 molecule as a whole does not dissociate [13] but in these circumstances the π-component of the double bond evidently ruptures, as a result of which various addition reactions (hydrogenation, polymerization, etc.) become possible. Here, as in the previous case, sharing of electrons probably takes place by means of the anti-bonding π-orbitals of the ethylene. There are also quantitative data in favour of the assumption of "dative loosening" of bonds undergoing activation by electrons of the active centre. Thus, if the energy of dissociation D of a hydrogen molecule in the ground state $(1s\sigma)^2$ is 4·74 eV and the equilibrium internuclear distance R_0 =0·74 Å [14], then for H_2^- $(1s\sigma)^2(1s\sigma^*)^1$ D=2·4 eV and R_0=0·86 Å [15]. These figures clearly indicate weakening of the H—H bond, with the anti-bonding molecular orbital in some way included in the general bonding.

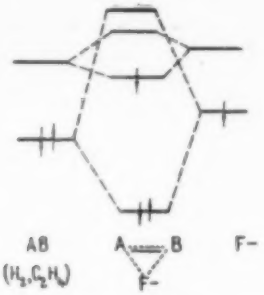

FIG. 1. Scheme of molecular levels of an F-centre—molecule AB complex (H_2—a pair of σ-electrons, C_2H_4—a pair of π-electrons, F denotes an F-centre).

Hence it may be considered that when a molecule AB(H_2, C_2H_4 etc.) approaches a defect of the F-centre type levels arise corresponding to sharing of electrons of AB and the F-centre in accordance with the qualitative scheme shown in Fig. 1. In a system of three centres,

not disposed along a straight line there is only one bonding level hence the spare electron is "dislodged" on to the anti-bonding level of the complex, the molecular orbital of which probably embraces all three centres, thus bringing about weakening of the A—B bond.

In conformity with the Alfin polymerizarion system it may be assumed that on crystallization of an alkali metal halide MX under the conditions of the Wurtz reaction ($\dot{M}+RX \rightarrow M^+X^- + M^+R^-$, where M is an alkali metal, X is halogen and R is alkyl), in the presence of M^+R^- adsorption of M^+ on the ionic lattice obviously takes place in accordance with the scheme shown in Fig. 2. The carbanion R^- is then localized at an anionic vacancy, giving a U'-centre *

* H^- in an anionic vacancy is a U-centre according to Seitz. We designate a U'-centre as R^- in the field of an anionic defect (here and subsequently we are discussing surface electron defects).

(in the formation of an impure crystal a U'-centre can also be formed within the crystal). It should be noted in this connection that in the Wurtz reaction a deeply coloured salt often precipitates (for example blue-black NaCl from the reaction Na+RCl). Specific investigations of such coloured precipitates have evidently not been carried out. We assume that such coloured crystals exert an effect on the course of reactions involving electron "transfer". These views are supported by the statement [16] that ethylene polymerizes on a K—KCl mixture with formation of a small quantity of solid polymer, and also by the above-mentioned data on polymerization in an Alfin system in the absence of sodium isopropylate. It is known also [3] that commercial, granulated NaCl exhibits little activity when introduced into the system but the finely crystalline NaCl obtained from a Wurtz reaction forms a very effective catalyst. We have found that coloured NaCl from a Wurtz reaction is a catalyst for the polymerization of acrylonitrile, methyl methacrylate and styrene, giving solid polymers.

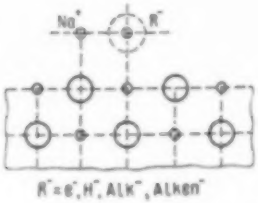

FIG. 2. Scheme of formation of an impurity crystal with U'-centres.

From the above picture of the chemisorption of a stoichiometric excess of an "impurity" on a lattice it is seen that an already formed M^+ cation is chemisorbed most readily and not M with its unpaired electron, in as much as in the first case the electron is transferred to the defect by means of the associated R^- particle, and in the second case it is transferred indirectly, with ionization of the M atom in the field of the lattice.

From this point of view the presence of an ionic alcoholate obviously makes possible the formation of a mixed crystal $Na^+Cl^- - Na^+OR^- - Na^+R^-$. It should be noted here, however, that the greater the affinity of R for the electron, the more readily a mixed crystal with U-centres probably forms. In the series of radicals with odd numbers of carbon atoms, $\dot{C}H_2$ (I), $\dot{C}H_2\dot{C}H\dot{C}H_2$ (II), $\dot{C}H_2\dot{C}H\dot{C}H\dot{C}H\dot{C}H_2$ (III) etc. the affinity for electrons increases monotonically [17] (for example, I—25, II—48 kcal/mole etc. [17]). Possibly these considerations have some bearing on the lower activity of an Alfin catalyst containing only "amylsodium" (in the absence of propylene).

If there is a molecule with π-electrons, for example butadiene close to an active centre such as a U-centre, then sharing of one of the electrons of R^- (in the field of the defect) is possible, by means of the system of π-electrons of the two molecules (R^- and C_4H_6). Also the first anti-bonding molecular orbital of butadiene evidently takes part in the sharing. The "nodal" plane of this

orbital is distributed between the first, second, third and fourth atoms of the hydrocarbon, leading to 1,4-activation of the π-system and to the possibility of formation of a σ-bond with the terminal atom of the R^- group. In this case an active "end", identical with the original, is again formed and R becomes the end group of a "polymer" (1,4-polybutadiene). It should be pointed out that the olefine and diolefine have a close π-electron configuration (in contrast to the radicals I, II, III—above) so that it must be the first anti-bonding level that takes part in the sharing of the extra electron, which is a prerequisite for activation with respect to addition, i.e. for the possibility of polymerization. This is perhaps reflected in the fact that the usual monomers are vinyl derivatives and dienes (and are rarely allylic compounds). From this point of view the reactivity of monomers must obviously be correlated with parameters that characterize "excited" states of the monomers (the energy of singlet-triplet excitation, the energy of the first unoccupied molecular orbital, the electron affinity of the monomer, etc.).

Morton [3, 4] found that the nature of the alkali metal halide has a substantial effect on the yield of polymer. This effect is normally connected with the dimensions of the cation and anion, which, it is suggested, characterize the surface geometry. Thus salts with a lattice constant $a < 2{\cdot}75$ Å cannot form active catalysts but salts with $a = 2{\cdot}81$–$3{\cdot}29$ Å are active catalyst components. The most effective salts are KCl, NaBr, NaCl and KBr. These data are in remarkable agreement with the experimental energies of ionization of the *F*-centres (see Table 1) for the corresponding halides, which leads to the conclusion that the activation energy of the centre is important.

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TABLE 1. EXPERIMENTAL VALUES OF THE IONIZATION ENERGY OF *F*-CENTRES

Salt	*E* (eV)	Salt	*E* (eV)	Salt	*E* (eV)
LiF	5·0	LiCl	3·1	LiBr	2·7
NaF	3·6	NaCl	2·7	NaBr	2·3
KF	2·7	KCl	2·2	KBr	2·0
		RbCl	2·0	RbBr	1·8
		CsCl	2·0		

From this it is seen that *F*-centres are stronger electron donors than even the most active alkali metals (Li—5·40, Na—5·14, K—4·34, Rb—4·17 and Cs—3·39eV [18]).

The exceptionally high initiation rate in the Alfin system must be connected with the unique electron donor properties of *F*-centres.

Vinyl monomers with functional groups, on sharing the unpaired electron, are obviously reduced because they do not polymerize under the normal Alfin polymerization conditions. With regard to the stereoregularity of polymers

prepared on Alfin catalysts, it has been established [19] that a solid phase is necessary in principle for the preparation of crystalline polymers. The clear hexane layer over a settled catalyst deposit on its own did not initiate the polymerization of styrene, but when a sufficient amount of solid phase was redispersed in it a high yield of polystyrene of moderate crystallinity was again obtained. In general, whereas in hexane, benzene and cyclohexane crystalline polystyrene was obtained, in ether, dioxan and dimethoxyethane the polymer was amorphous. Addition of ether to the hexane resulted in a reduction in crystallinity in proportion to the quantity of ether added. On the other hand the use of "ethereal" media markedly increased the polymerization rate, but even at low temperatures isotactic polystyrene was not obtained [19].

These facts can be interpreted in the following way. It is known that alkali metals dissolve in "ethereal" solutions of substances having affinity for an electron (the term "ethereal" media denotes solvents containing a hetero-atom with an unshared pair in its molecule). The uniqueness of these media is probably caused by the ability of ether-type molecules to co-ordinate themselves readily about M^+ (M=Li, Na,—) and the "dislodging" and subsequent transfer of the electron are facilitated by stabilization of M^+ in the form of an etherate with the gain of the energy of dipole-ion interaction in addition to the energy of the co-ordination bond. The co-ordinating power of these molecules is so great that sometimes even in the absence of a suitable acceptor molecule in the system partial solution of the alkali metal takes place [20, 21]. Thus recently a paper appeared [21] on the use, as a polymerization catalyst, of a "blue solution of potassium in tetrahydrofuran" where evidently complex molecules of the type $K(OR_2)_n$ occur. Here the unpaired electron is in all probability "dislodged" by the unshared pair of the oxygen atom in the *p*-orbital. As a result of such co-ordination the electron donor effect of the metal atom is greatly increased (the sp-interval for K (1·6eV) is less than for Li (1·8eV) or Na (2·1eV) so that the formation of a complex with potassium is understandable from this point of view). In view of the foregoing we suggest that a "colour centre", similar in electronic structure to an alkali metal atom, in an "ethereal" medium co-ordinates about itself molecules of the solvent. Then the unshared pair of the oxygen atom "goes" to a suitable level of the electron defect and the unpaired electron of the defect is "dislodged" to a higher level. Then, naturally, the transfer of the unpaired electron to the double bond of the monomer is facilitated and the initiation rate must increase markedly (this is quite analogous to the qualitative scheme of Fig. 1, where the pair of π-electrons plays the part of the unshared pair of the oxygen atom).

The very fact of the marked deterioration in stereo control in the presence of "complexing" agents leads to the conclusion that the electron defect takes part in initiation and propagation and when it is blocked the conditions for stereospecific synthesis are impaired. This may be connected with the possibility of partial displacement of the carbanion from the defect by an ether molecule, which naturally results in a lessening of stereo control in view of the decrease

in the effect of excitation contributed by the lattice, in the field of which the choice of the most suitable stereoconfiguration obviously takes place.

In view of the above considerations we suggest that it would be of interest to make a systematic investigation of the chemisorption and catalytic activity of various coloured crystals in relation to various reactions (including polymerization). Experiments on the effect of chemisorption on the electrical conductivity, optical and magnetic characteristics of coloured crystals, and also experiments on the effect of irradiation (with long wave light corresponding to the *F*-absorption bonds of the corresponding crystals) on chemisorption and catalytic activity, we feel should enable more direct conclusions on the mechanism of catalytic reactions to be drawn. In this connexion the well studied and simplest structured coloured crystals of the alkali metal halides are particularly interesting.

CONCLUSIONS

The mechanism of heterogeneous, Alfin-type catalytic polymerization is examined from the point of view of the suggestion that the active centres of the catalyst are electron defects of the "colour centre" type. Dative interaction in which the unpaired electron of the active centre and the anti-bonding molecular orbital of the bond undergoing activation play an essential part in the activation of the monomer.

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THE ROLE OF SURFACE ELECTRON DEFECTS IN HETEROGENEOUS CATALYTIC POLYMERIZATION—II. CATALYST SYSTEMS OF THE ZIEGLER-NATTA TYPE*

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THE heterogeneous catalytic polymerization of α-olefines is of great industrial importance. For this reason numerous attempts have been made to explain the nature of the "complex" catalysts used [1, 2]. In spite of the fact that all the authors, independently of the polymerization machanism that they suggest, connect the high effectiveness and stereospecificity of the catalysts with the heterogeneity of the catalyst system, the investigations are carried out within the framework of schemes of known homogeneous processes, hence the taking into account of the specific features of heterogeneity is made difficult. The unsatisfactory nature of such an approach is shown by the coexistence of explanations of one and the same process from the points of view of anionic-co-ordination [3, 4], cationic [5, 6], radical [7, 8] and radical-ion [9, 10] mechanisms. Moreover assumptions are often made that are by no means obvious, when applied to other similar catalyst systems. Such mechanisms naturally cannot embrace all the existing experimental material and are not of any practical value. Thus Gaylord and Mark [1] mention more than 250 different Ziegler-type catalysts for the polymerization of ethylene alone. Among them are systems that are quite unexpected from the point of view of known mechanisms, for example "special" titanium dichloride, mixtures of boron halides with alkali-metal aluminium hydrides, combinations of $Ti+TiCl_4$, $Al+CoCl_2$, a Ti-Al alloy + alkyl chlorides etc. All this brings about the necessity of seeking another approach to the problem of the catalytic activity of heterogeneous, "complex" catalysts. Such an attempt is made in this communication.

In the previous paper [11] we put forward a suggestion which as far as the heterogeneous polymerization of unsaturated molecules is concerned reduces to the necessity of attraction of the anti-bonding molecular orbitals to the monomer bond undergoing activation, for the sharing of electrons donated by an active centre of the catalyst. On the basis of this suggestion we attributed the catalytic activity of certain heterogeneous catalysts to the presence in them in one form or another, of electrons localized in defects of the "colour centre" type [11]. From the point of view of the inclusion in the bonding, in the transition

* Vysokomol. soedin. **2**; No. 4, 535–540, 1960.

state, of anti-bonding molecular orbitals of the monomer, the reactivity of the monomers should obviously be correlated with such parameters as the energy of singlet-triplet excitation, the energy of the first unoccupied molecular orbital, the affinity of the monomer for electrons etc.

Polymerization on Ziegler ($TiCl_4+AlR_3$) and Natta ($TiCl_3+AlR_3$) catalysts is usually carried out in an inert hydrocarbon. In systems of the type of $TiCl_4+AlR_3$ the homogeneous, stoichiometric reduction reaction evidently takes place first [1]:

$$TiCl_4+AlR_3 \longrightarrow TiCl_3+AlR_2Cl+\dot{R} \quad (R=C_2H_5)$$

with the formation of crystalline titanium trichloride. The latter has a hexagonal lattice and the surface of the layer probably consists of chlorine anions (excluding defects). We suggest that the catalytic activity of systems of the type of Ziegler–Natta catalysts must be due to the presence of impurity crystals containing surface electron defects of the "colour centre" type. One of the possible means by which they are formed concerns the chemisorption of the metal alkyl on the ionic lattice of $TiCl_3$. In this case an atom of aluminium in the aluminium trialkyl interacts, evidently, with the surface Cl^- anions, which is brought about by the greater affinity of the aluminium atom for chlorine than for the carbon atom in the alkyl group. Thus the ionic lattice is finished off by Al^+R_2 cations formed from AlR_3 in the field of the surface Cl^- anion. As a result an impurity crystal with an over-all positive charge is formed. In so far as such crystals are essentially ionic systems that preferably remain electrically neutral this requires the "formation", in accordance with the above-mentioned process, of an anionic vacancy ("hole") near which an R^- carbanion is localized. In this way on the one hand the anionic vacancy is "satisfied", and on the other hand the unstable, aliphatic anion is stabilized. This type of defect may be called a U′-centre. Thus the active centres of systems of the type of Ziegler–Natta catalysts may be surface electron defects of the F-, U- and U′-centre type [11]. Naturally at points where there are "ready-made" defects (e.g. dislocations appearing at the surface) chemisorption of the metal alkyls is facilitated and therefore polymerization at these points would be expected in the first place. Other methods of forming electron defects are also possible, for example the mechanical grinding of ionic crystals, grinding in the presence of suitable metal alkyls or in the monomer [12–14, 17], irradiation with electrons, neutrons and X-rays, electrolysis etc.

Some special features of the use of these catalyst components should be noted. The higher transition halides of the type of $TiCl_4$ and VCl_5 differ substantially from other transition and non-transition halides in that under normal conditions they are mobile, volatile liquids, readily soluble in nonpolar, organic solvents. This suggests that they have a covalent structure in contrast to the other halides (that are high melting insoluble in organic solvents etc.). Obviously this difference can be explained by the fact that in the $TiCl_4$ molecule as well as four tetrahedral hybrid σ-bonds, delocalized π-bonds can also exist, resulting from

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the sharing of the unshared pair of the chlorine atoms through the medium of an unoccupied orbital of the titanium atom, of suitable symmetry. A theoretical-group examination shows that all nine d^5sp^3 orbitals could be used for this, so that a close tight molecular envelope results, which is in agreement with the low intermolecular interaction observed experimentally. The majority of the metal alkyls of the second and third groups also are (in principle) covalent compounds. Thus reduction of $TiCl_4$ by covalent metal alkyls is facilitated by the fact that in place of the covalent bond between titanium and chlorine, the more typical ionic bond for the latter in Al^+Cl^- is formed, and the strengths of the Ti—C and Al—C bonds are evidently of the same order. It should be noted however that orbitals of an essentially *d*-character, for example the sd^3 orbitals of the Ti atom, in virtue of their geometry are probably poorly adapted for the formation of bonds with sp^3 orbitals [16], hence homolytic rupture of the Ti—C bond would be expected, as is observed experimentally. Consequently covalent chlorides ($TiCl_4$, VCl_5, $MoCl_6$, etc.) are readily reduced by metal alkyls and are more effective catalyst components (as regards rate) than the ionic chlorides. However the conditions for stereo-control are impaired in this case [1], evidently as a result of the formation of an impurity crystal with a highly distorted lattice resulting from the inclusion (at the surface and internally) of various "impurities" (for example AlR_2Cl, AlR_3 etc.). If however a "ready-made" ionic chloride is used (transition or non-transition) then an impurity crystal is very readily formed, evidently on chemisorption of an ionic metal alkyl [11] (for example Li^+R^-, Na^+R^-, etc., where R^- is small).

As regards a definite mechanism of initiation and propagation of polymer chains, it consists, schematically, in the following. If there is a molecule with π-electrons close to an anion R^-, localized near an anionic vacancy (U′-centre) sharing is possible of one of the electrons of the anion (in the field of the decect) in which the π-system of the olefine takes part. This leads to loosening of the double bond of the monomer and to the possibility of formation of a σ-bond between a carbon atom of the anion and a neighbouring C-atom of the monomer. In this process the anion first becomes the end group of a growing polymer chain and an active centre R^- is formed anew, localized near an anionic defect (here R is increased by one monomer unit). It should be pointed out that in the sharing of an electron through the mechanism of dative interaction the barrier to internal rotation about the double bond is lowered as a result of the loosening. This enables the alkyl group od the olefine to become easily orientated in a field of even a low excitation, which in this case can be the repulsion of the surface atoms of the lattice. In this field evidently the choice of stereo-configuration of the chain is also made, which corresponds to the minimum potential energy of the excitation field (for example the choice of the isotactic configuration takes place).

These suppositions enable the main experimental data in the field under examination to be interpreted. Thus it is quite understandable why the addition of only 0·04 mole of $Al(C_2H_5)_3$ to crystalline $TiCl_3$ leads to the stereospecific

polymerization of propylene at a satisfactory rate [17], whereas "pure" $TiCl_3$ obtained from $TiCl_4$ by reduction with hydrogen is inactive. The "induction" period noted by Natta [17] when using $TiCl_3$ of large particle size is usually explained by the assumption that the reaction (the chemisorption of the metal alkyl) is limited initially to the outer surfaces of the macrocrystal and only after a certain time, connected possibly with breakdown of the crystals along the planes of cleavage, is a steady-state process realized. When $TiCl_3$ is prepared from $TiCl_4$ by reduction with hydrogen the formation of electron defects is possible in principle by the ionization of H atoms and subsequent chemisorption of H^+ on the ionic lattice, with the formation of an *F*-centre. However the ionization potential of the hydrogen atom (13·5eV) is considerably higher than that of the alkali metals (3–5eV), hence the formation of electron defects of this type is probably hindered. This is, perhaps, the reason why $TiCl_3$ obtained by the reduction of $TiCl_4$ by hydrogen is inactive. However on reduction by metal alkyls, hydrides, powdered metals etc., chlorides of low valency can contain these electron defects. In all probability this does not explain the high activity of "special" $TiCl_2$ [18–20], obtained from $TiCl_4$ by reduction with metal alkyls. It is not impossible that by simple treatment of ionic halides with the vapours of the corresponding metals or their alkyls, fairly effective catalysts for the polymerization of various monomers could be obtained. In contrast to U- or U′-centres typical "radical-ion" polymerization would be expected in polymerization on an *F*-centre, analogous to the copolymerization of styrene and methyl methacrylate in the presence of lithium* [21–23]. We have examined the electronic structure of the *F*-centre–olefine complex in a qualitative manner [11]. The olefine appears in this complex in a saturated form $(C_2H_4)^-$ (a negatively charged radical). Then interaction with a second molecule of olefine will result in the sharing of this unpaired electron by means of dative interaction and only after the formation of σ-bonds between the reacting molecules will a radical ion arise, localized at the anionic end at the defect or "hole". This position is completely analogous to initiation by a negatively charged naphthalene radical $(C_{10}H_8)^-$. Thus conditions are created for simultaneous chain growth "in two directions", by the ordinary free-radical and anionic routes. In our opinion in both cases the mechanism of initiation consists in the loosening of the double-bond of the olefine brought about by the sharing of an unpaired electron of radical $\dot{R}$ or of one of the electrons of the anion R^- through the medium of an antibonding π-molecular orbital of a second molecule of the olefine. The difference between these mechanisms can be attributed, for example, to the unequal electron-donor characteristics of the radical and anionic "ends". Thus the ionization potential of CH_3 is 9·50eV (243kcal) but for $(CH_3)^-$ it is only 1·1eV (25·5kcal) [24]. This difference is in accord with the rates and activation energies of the two processes (the effect of the associated cation should also be taken into account in the mechanism of initiation by R^-).

*Simultaneously this idea was suggested and verified experimentally in reference [15].

The catalytic activity of other modified Ziegler catalysts can be explained in a similar way. Let us examine, for example, the system $TiCl_4+NaH+$ +anthracene or $TiCl_4+NaH+AlCl_3$ [1]. Sodium hydride is an ionic compound hence the conditions for the reduction of $TiCl_4$ are unfavourable, however a solution of anthracene in benzene can evidently take part in the heterogeneous reaction $H^-_{crystal} + An \rightarrow An^- + \dot{H}_{solution}$ (where An is anthracene), and then the homogeneous reduction of $TiCl_4$ by hydrogen is possible. The anthracene anion serves subsequently as the carrier of an electron to the defect formed by chemisorption of Na^+ on the ionic lattice of $TiCl_3$. As regards the second system, here evidently the mixed crystal $NaH-AlCl_3$ is first formed in which the hydrogen does not occur in the purely ionic state (H^-) and the conditions for the reduction $TiCl_4$ are again improved. A similar approach can be made to an explanation of the activity of such combinations as Ti—Al alloy + an alkyl chloride, $CoCl_2+LiAlH_4$, $CoCl_2+Mg$, $CoCl_2+Al$, $TiCl_4+Al(OR)_3+AlCl_3$ [1], or the catalyst obtained by the decomposition of CH_3TiCl_3 in solution in an inert hydrocarbon [25].

The hypothesis developed here can be used to explain experimental data on the increase in molecular weight of the polymer and in some cases also in polymerization rate on the introduction of additives (amines [26, 27], ethers, sulphides [28]). In this case it is probably necessary to take into account co-ordination of the "ether" molecule about the electron defect, as a result of which conditions are created for the "displacement" of an unpaired electron at a higher atomic or molecular level. Thus the ionization potential of the co-ordinated active centre is evidently decreased and this also facilitates the subsequent sharing of the electron. The increase in rate of the process can also be attributed to the ability of the "ethereal" additive (especially of amines [26]) to become co-ordinated with $TiCl_3$. This latter fact facilitates the breakdown of the crystals along the planes of cleavage, with a consequent increase in the number of active centres, and consequently "displacement" of an unpaired electron of $TiCl_3$ at a higher level.

From the present point of view compounds that are reduced in the presence of Ziegler catalysts under normal conditions, especially nitro-compounds [29] and polar vinyl monomers [1], should inhibit the polymerization of olefines on "complex" catalysts because of their attraction for electrons in reduction. This has been confirmed by experiment [1]. For example HCl is split off from vinyl chloride in the presence of Ziegler catalysts in the medium of an unsaturated hydrocarbon [1]. The preferential reduction of the polar in comparison with the olefinic double bond may be attributed to the lower relative disposition of the first unoccupied molecular level in the first case, which evidently gives rise to the possibility of excitation of the unshared *p*-pair of the hetero-atom (O, S, Cl) at an intermediate molecular level (known in electron spectroscopy as h-π excitation). This is reflected in the fact that polar double bonds are always reduced more readily than isolated olefinic bonds, as is well known in practice in reduction, for example, with lithium aluminium hydride [30]. Replacement

of the inert hydrocarbon by an "ethereal" medium probably leads to a change in the polarity of the C—X bond (X is the hetero-atom) in the monomer as a result of co-ordination or dipole-ion interaction. This hinders reduction of the functional groups and leads to the possibility of sharing of an electron of the π-bond, i.e. of its reduction. All this is reflected to some extent in the fact that polar vinyl monomers polymerize only in "complexing" media [31].

It is known that coloured crystals of the alkali metal halides can be decolorized by long-wave irradiation, corresponding to the ionization energy of the *F*-centre. It may be thought from this that the catalytic and chemisorption activity of such coloured crystals would be affected substantially by the action of light of certain wavelengths. This supposition is quite true of the catalytic activity of Ziegler precipitates and it is most probable that the increase in polymerization rate on irradiation arises from the possibility of optical excitation of the electron to a higher level.

The authors express their sincere thanks to G. A. Razuvaev and T. K. Rebane, and also to V. A. Kabanov and A. A. Arest-Yakubovich who took part in discussions on this work and made a number of valuable observations.

CONCLUSIONS

Heterogeneous polymerization in the presence of Ziegler-type catalysts is examined. It is suggested that impurity crystals are formed in the system, that contain surface electron defects of the "colour centre" type. Activation with respect to addition reactions (i.e. initiation) is brought about by the mechanism of dative interaction in which anti-bonding molecular orbitals of the monomer molecule and suitable orbitals of the electron defect take part.

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THE GLASS TEMPERATURE OF CRYSTALLINE POLYMERS*

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USUALLY the melting point is taken as the basic temperature characteristic of crystalline polymers, being chosen because the whole complex of properties (mechanical strength, high deformability etc.) inherent in these materials is maintained up to the melting point of the crystallites. However, as we have shown previously [1], the glass temperature of an amorphous polymer serves as a valuable characteristic for the determination of the working temperature range of the same polymer in the crystalline state. At the present time in view of the wide, practical application of crystalline polymers, determination of the working temperature range is particularly important.

This paper is devoted to the determination of the temperature characteristics of polypropylene.

Polypropylene was prepared in the laboratory with various catalyst systems: $TiCl_4+Al(C_2H_5)_3$; $TiCl_3+Al(C_2H_5)_3$; $TiCl_3+Al(i-C_4H_9)_3$ and $CrO_3/Al_2O_3.SiO_2$ was used as the material for investigation. The samples differed in molecular weight and in the ratio of the fractions.

The original products were fractionated by extraction with ether and *n*-heptane at the boiling points of the solvents. The amorphous polypropylene (fraction I) was separated from solution in ether by precipitation with methanol. Fraction II, consisting mainly of low-molecular, crystalline polymer was precipitated from the heptane extract by acetone. The polypropylene that is insoluble in both solvents (fraction III) is the isotactic product [2].

The intrinsic viscosities of solutions of polypropylene in decalin at 120°C were determined, for calculation of the molecular weight of the fractions. Fractions with following intrinsic viscosities were used in the experiments: 0·075; 0·13; 0·15; 0·2; 0·36; 0·4; 0·5; 0·66; 0·8; 0·96; 1·25; 1·38.

For determination of the glass temperature the samples were subjected to testing on a dynamometric balance under loads of 0·3, 15·9 and 510 kg/cm². The samples were prepared in the form of tablets by pressing at 160° and 15 kg/cm². In the thermomechanical tests the deformation occurring in the samples under the appropriate load in 10 sec was measured. The rate of heating was 0·7–1° per minute. The results are shown in Fig. 1–3. The abscissa represents temperature and the ordinate the percentage deformation. Figure 1 shows the

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thermomechanical curves of the first polypropylene fractions. Beginning with a molecular weight corresponding to an intrinsic viscosity of approximately 0·1 the curve shows three sections, corresponding to the three physical states of the amorphous polymer. The region of high-elastic deformation lies between the glass temperature of −10 to −15° (which is independent of molecular weight) on the left, and the flow temperature on the right, which normally increases with increasing molecular weight [3] and decreases with increase in load (see Figs. 1a and b).

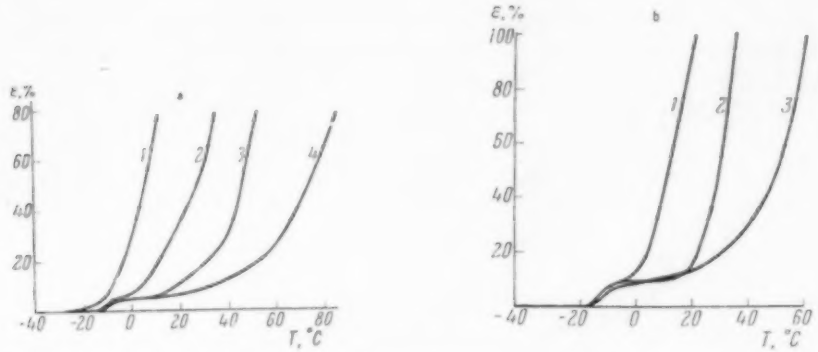

FIG. 1. Thermomechanical curves of atactic polypropylene. (a) Load 0·3 kg/cm². Intrinsic viscosity of polypropylene: (1) 0·075; (2) 0·13; (3) 0·2; (4) 0·8. (b) Load 15·9 kg/cm². Intrinsic viscosity of polypropylene: (1) 0·36; (2) 0·66; (3) 1·28

The thermomechanical curve of crystalline polypropylene (Fig. 2, curve 1) shows that over a wide range of temperature, in contrast to atactic polypropylene the sample undergoes practically no deformation and only at the melting point does it pass to the viscous-flow state. However, if the polypropylene is made amorphous (by heating above the melting point then cooling rapidly) a region corresponding to the high-elastic state appears in the thermomechanical curve (Fig. 2, curve 2).

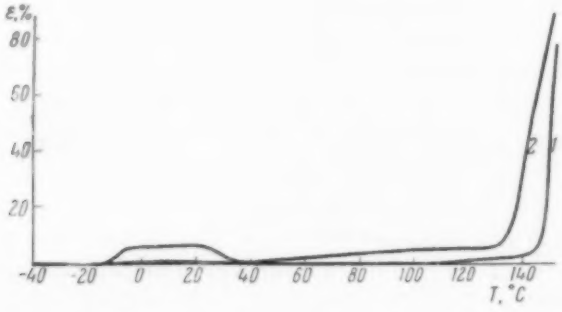

FIG. 2. Thermomechanical curves of polypropylene. Load 0·3 kg/cm²:(1) crystalline polypropylene; (2) amorphous polypropylene.

As in the case of atactic polypropylene the high-elastic region begins at $-10°$ but on continuing to increase the temperature the deformation decreases as a result of transition of the polymer from the amorphous to the crystalline state. This property is explained by the regular structure of the polypropylene chains, as a result of which the polymer is able to crystallize again. On melting, the configuration of the chains becomes less ordered but the regular sequence of the asymmetric carbon atoms in the molecule is maintained. Rapid cooling of the melt hinders the process of ordering of the chains and in the glassy state they maintain the shape that they acquired in the melt. Crystallization occurs only above the glass temperature, where the mobility of the segments is sufficiently high. Investigation of the thermomechanical properties of an amorphous sample is therefore one of the methods of determining the glass temperature of a crystallizable polymer.

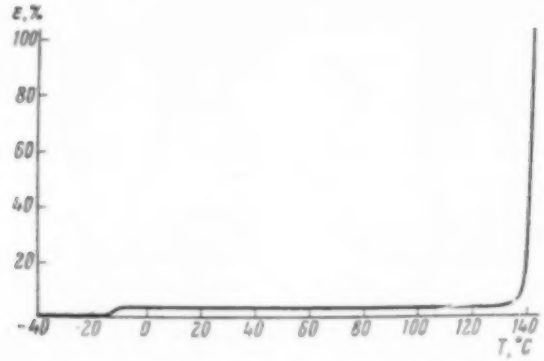

FIG. 3. Thermomechanical curve of crystalline polypropylene. Load 510 kg/cm².

The glass temperature of crystalline samples was determined directly with loads of the order of hundreds of kg/cm² (see Fig. 3). In the temperature region corresponding to the high-elastic state of amorphous polypropylene there is a low, but distinct, plateau in the thermomechanical curve of the crystalline sample. Consequently the properties of crystalline polypropylene do not remain unchanged over a wide range of temperatures. Above $-10°$ the thermal-movement of the segments increases and even in the crystalline state the chains acquire a certain mobility, giving an indication of the flexibility of the molecular bundles that make up the crystalline structure. However the flexibility under these conditions is very low and is detectable only under the action of high stresses. Below $-10°$ this movement is frozen and the polymer becomes brittle.

Thus in a certain sense the conception of glass temperature is still applicable to the crystalline polymer and it coincides with the glass temperature of amorphous polypropylene.

Uniaxial extension of films on a Polyan'i-type dynamometer enabled the glass temperature of polypropylene to be determined by the dynamic method.

In these experiments the films used were made by pressing at 50 kg/cm² and a temperature of 170°. The samples were stamped out to give a working portion of dimensions 10 × 2 mm. The rate of extension in all cases was 0·083 cm/sec. The results are shown in Figs 4 and 5 where the abscissa represents the relative deformation, expressed as a percentage, and the ordinate represents the stress calculated with respect to the initial cross-section of the sample (σ).

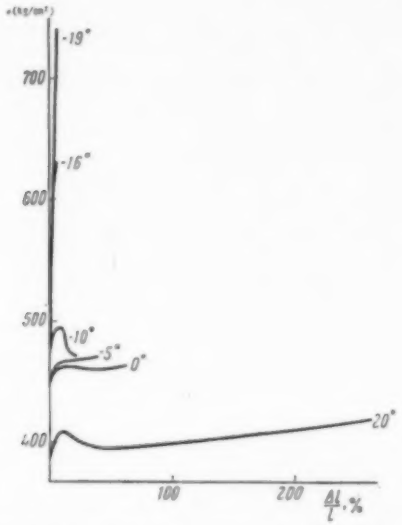

FIG. 4. Extension curves of isotropic polypropylene films (the temperature at which extension was carried out is indicated on each curve).

All unorientated, crystalline polymers below the glass temperature rupture in the region of low Hookian deformation. Above this temperature where rearrangement of the structure and orientation of the chains in the direction of the applied stress is possible, marked elongation occurs (Fig. 4), shown by the horizontal sections of the curves which correspond to the appearance of "necks" i.e. to the transition of the sample to the orientated state. With increasing temperature a tensile strength of the order of 400 kg/cm² and an elongation of approximately 300 per cent is found, which is characteristic of articles made from polypropylene.

In the temperature interval from −10° to −15° the phenomenon of "cold drawing" of polypropylene disappears and it becomes brittle.

Orientation gives rise to anisotropic properties. Repeated extension along the axis of orientation can be carried out under stresses greater than the original stress because the tensile strength of the film increases 2–3 times after orientation. The elongations are from 30–50 per cent (Fig. 5a) and occur only at temperatures above 15°. Extension of the films in the perpendicular direction is possible at temperatures as low as −65° (Fig. 5b). The tensile strength in these

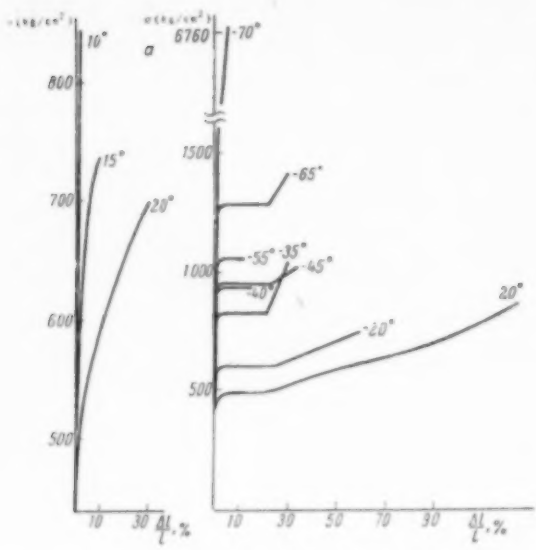

FIG. 5. Extension curves of orientated films: (a) along the axis of orientation; (b) perpendicular to the axis of orientation.

circumstances increases to about 1,000 kg/cm². Thus the range of working temperatures, which is limited for the isotropic films by the glass temperature of −10 to −15° is considerably widened, and the glass temperature itself is lowered to −65 to −70°, i.e. to a temperature typical of other polymeric hydrocarbons with flexible chains. The glass temperature of polypropylene is probably controlled by its special structural features. We now know that crystalline polymers are not simply systems of unordered, entangled chains with isolated regions of crystalline order but consist of a continuous series of increasingly complex structures; aggregates in bundles, then in flat bands, forming spherulites, and finally single crystals of microscopic dimensions [4]. Possibly the glass temperature of crystalline polypropylene is connected with just this appearance of ordered, secondary structures and its marked fall on orientation with the breakdown of these structures. It is characteristic of amorphous polymers that the glass temperature does not fall on orientation, and in some cases it even increases (mechanical vitrification) [5].

In conclusion it is our pleasant duty to express sincere gratitude to B. A. Krentsel' for assistance and interest in this work.

CONCLUSIONS

(1) The glass temperature of polypropylene has been estimated by three independent methods; by deformation of crystalline polypropylene under high mechanical stress, by thermomechanical testing of amorphous polypropylene and by a study of "cold drawing" in the stretching of films.

(2) The thermomechanical properties of atactic polypropylene have been investigated and it is shown that the glass temperatures of crystalline and non-crystalline polypropylene coincide.

On the basis of the experimental results obtained the conclusion is drawn that the idea of a glass temperature in the assessment of the properties of crystalline polymers plays as important a part as it does for amorphous polymers. Hence in determining the working temperature range of crystalline polymers it is necessary to establish two characteristic values, the glass temperature and the melting point. Outside the limits of these temperatures crystalline polymers loose their specific mechanical properties to a considerable extent.

(3) A preliminary orientation of crystalline polypropylene enables the working temperature range to be extended.

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INVESTIGATION OF THE MECHANISM OF AGEING OR SYNTHETIC FIBRES—I. A STUDY OF THE THERMAL AND THERMAL-OXIDATION REACTIONS OF POLYAMIDES AND POLYAMIDE FIBRES*

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IT is well known that all fibres and articles made from fibres undergo ageing processes in use, and this leads to deterioration of their physico-mechanical properties. This is of particular importance in the case of fibres used for technical purpuses.

The deterioration in properties of such articles in use is the result of the occurrence in the polymers themselves, and in the fibres, of two types of processes, chemical and structural.

The chemical processes, which are brought about by the action of heat, light, atmospheric oxygen and other factors, involve changes, in the chemical composition of the polymer resulting from the elimination of volatile decomposition products and the addition of oxygen.

The structural processes, arising from the action of these same factors, involve phase transitions (transition from the crystalline to the amorphous state and the converse) and changes in orientation of the polymer molecules.

Both processes can occur simultaneously under actual working conditions. Naturally if is necessary to know the nature of the phenomena and the mechanism of each process in order to prevent or minimise the occurence of such processes.

Consequently a study of the mechanism of ageing of polymers and synthetic fibres is of great theoretical and practical importance.

One of the important factors that accelerate the ageing of heterochain polymers (polyamides and polyesters) is thermal oxidation, to which fibres and fibre-based products are most often subjected during use. In spite of the importance of this problem the ageing of polymers and synthetic fibres has been studied little.

The existing literature data [1–6] are insufficient for an understanding of the mechanism of the changes taking place in polymers and fibres under the action of high temperatures, light, atmospheric oxygen and others factors.

* Vysokomol. soedin. **2**: No. 4, 581–589, 1960.

In most of the papers known to us the loss of valuable properties of fibres and products made from fibres on ageing is noted, but there are hardly any from which any light could be thrown on the mechanism of the ageing processes, and for this reason there are no scientific princip'es underlying the choice and for this reason there are no scientific principles underlying the choice and application of the various materials used as stabilizers.

Achhammer and his collaborators [1] studied the effect of high temperatures and ultraviolet radiation on polyamides and found that at high temperatures gaseous and liquid products are formed among which were detected by mass-spectrometry, H_2O, CO, C_2H_5OH, CO_2 and hydrocarbons. The formation of considerable quantities of CO in the pyrolysis of polyamides was explained by the rupture of C—N bonds by a mechanism not established in that paper.

Gudman [5] investigated the thermal degradation of dibutyladipamide, as a model for nylon-66, in an atmosphere of nitrogen at 290° and 350°C, and found that the volatile breakdown products consisted of *n*-butylamide, CO, CO_2, C_4H_8, H_2, NH_3 and C_4H_{10}.

Rafikov and Sorokina [6] studied the chemical transformations of polyamides at temperatures in the region 300° and showed that the basic trends of the chemical transformations of these polymers at hight temperatures depend on their structure and on the experimental conditions. These authors observed depolymerization of the polyamide with separation of caprolactam as a result of intramolecular exchange reactions, taking place both at the terminal segments of the chain and at any point along the chain. Steiger [7] investigated the causes of yellowing of nylon and made the suggestion that this yellowing is caused by reactions of amino groups occurring at the ends of the molecular chains, which result in the formation of coloured products. Finally a number of authors have studied the effect of high temperatures on the properties of synthetic fibres [2, 8–11] and also changes in the properties of textile materials on weathering [11, 12].

The object of the present investigation is a study of some problems of thermal-oxidative breakdown of polyamides in the initial stages at temperatures close to those encountered in actual use.

METHOD*

For the study of the thermal and thermal-oxidation reactions in the ageing of polymers the following materials were investigated: polyhexamethyleneadipamide (PHMAA) and Anid fibre, and polycapramide (PCA) and Kapron fibre. For this purpose the special thermal-oxidation apparatus described by us previously [13] was set up.

The investigations were carried out at temperatures from 160° to 220°, in an atmosphere of nitrogen for the thermal degradation experiments and in air or oxygen for the oxidation experiments. The volatile decomposition

* Technician A. M. Glebova took part in the experimental work.

products evolved on heating these polymers and fibres were trapped by freezing in liquid oxygen.

For the polymers and their derived fibres treated in this way the following were determined: loss of weight due to volatile breakdown products, change in viscosity of 0·5% solutions in tricresol, changes in physico-mechanical characteristics and elementary composition.

The polymers were investigated in the original, unpurified state and after purification by reprecipitation from solution.

Preparation of samples. For the purification of PCA and PHMAA 1% solutions of these in formic acid were prepared. For precipitation of the polymers from solution water was added dropwise, with stirring. The precipitates in the form of a powder were filtered off, washed with distilled water at 50–60°, and dried first in a drying oven and then *in vacuo*.

RESULTS

(*a*) *Polycapramide.* The results of experiments on the thermal and thermal-oxidative treatment of reprecipitated and untreated PCA showed that on heating PCA at 170–200° for long periods volatile products are evolved. It was noted also that on heat treatment the viscosity of 0·5% solutions of PCA in tricresol increases (Table 1) and on thermal-oxidation it decreases. The changes in viscosity and weight of reprecipitated and untreated PCA during heat and thermal-oxidative treatment are shown in the table.

TABLE 1. EFFECT OF THERMAL AND THERMAL-OXIDATIVE TREATMENT ON PCA

Temperature (°C)	Time of heating (hr)	Original PCA				Precipitated PCA			
		in nitrogen		in oxygen		in nitrogen		in oxygen	
		Viscosity (η_{sp})	Change in weight (%)	Viscosity (η_{sp})	Change in weight (%)	Viscosity (η_{sp})	Change in weight (%)	Viscosity (η_{sp})	Change in weight (%)
Original		0·699	—	0·699	—	0·754	—	0·754	—
160	1	0·700	0·3	0·342	1·62	0·754	—	0·621	0·4
160	2	0·702	0·4	0·282	2·10	0·762	0·1	0·570	0·52
160	4	0·704	1·1	0·200	2·95	0·805	0·35	0·524	1·00
180	4	0·804	1·3	not observed	4·03	0·834	0·80	0·274	2·04

It is seen from the data in Table 1 and Fig. 1 that the viscosity of 0·5% solutions of reprecipitated PCA decreases considerably less than that of untreated PCA on thermal-oxidative treatment and this is probably connected with the presence of various impurities in the untreated material which accelerate the thermal-oxidative breakdown of PCA.

(*b*) *Polyhexamethyleneadipamide.* The experimental results showed that on heating PHMAA at 170° and 220° in an atmosphere of nitrogen the viscosity changes

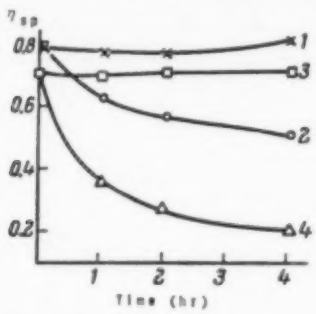

FIG. 1. Variation in viscosity of solution of PCA, subjected to thermal and thermal-oxidative treatment: (1) reprecipitated PCA in a current of nitrogen; (2) the same in a current of oxygen; (3) original PCA in a current of nitrogen; (4) the same in a current of oxygen.

present a complex picture. As Fig. 2 shows, the viscosity at first passes through a minimum and degradation, caused evidently by volatile impurities, predominates. For the unpurified polymer this minimum occurs earlier than for the reprecipitated material, possibly because of the greater content of volatile impurities in the unpurified polymer. The greatest evolution of volatile decomposition products, determined by the change in weight of the polymer, coincided with a sharp fall in viscosity.

It is seen from Table 2 that the greatest evolution of volatile products on heating at 200° in an atmosphere of nitrogen occurs after 1 hr in the case of the unpurified polymer and after 2 hr in the case of the reprecipitated material, corresponding to the viscosity minima of the curves of Fig. 2, and consequently the assumption made about the accelerating effect of volatile impurities on thermal degradation is confirmed. In conformity with this, considerably less change in weight is obserwed for reprecipitated PHMAA.

TABLE 2. CHANGE IN WEIGHT AND VISCOSITY OF PHMAA AFTER HEATING AT 200° IN NITROGEN

Time (hr)	Original PHMAA			Reprecipitated PHMAA		
	Viscosity (η_{sp})	Change in weight		Viscosity (η_{sp})	Change in weight	
		%	Period of observation		%	Period of observation
Original	0·735	—	—	0·772	—	—
1	0·572	3·3	3·3	0·712	0·9	0·9
2	0·650	5·38	2·08	0·665	3·4	2·5
3	0·745	7·28	1·9	0·804	4·75	1·35
4	0·672	9·28	2·0	0·732	6·12	1·73

Further heating of the polymers causes an increase in viscosity to a maximum, where evidently crosslinking predominates. On heating at 200° in an atmosphere of nitrogen the maximum for both the unpurified and reprecipitated polymer

is reached at the same time, after three hours' heating. The purer the polymer and the higher the temperature of heat treatment the higher is the viscosity maximum (Fig. 2).

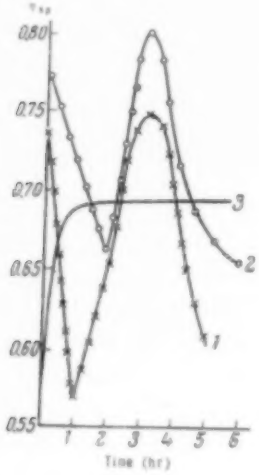

FIG. 2. Variation in viscosity of solutions of PHMAA and Anid fibre after heating at 200°: (1) original PHMAA; (2) reprecipitated PHMAA; (3) Anid fibre.

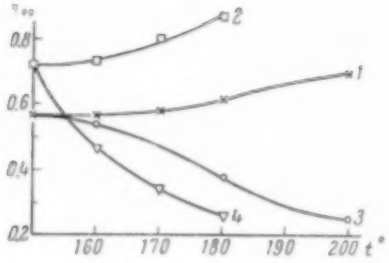

FIG. 3. Variation in viscosity of solutions of polyamide fibres subjected to thermal and thermal-oxidative treatment: (1) Anid in a current of nitrogen; (2) Kapron in a current of nitrogen; (3) Anid in a current of oxygen; (4) Kapron in a current of oxygen.

On further heating, a small drop in viscosity occurs followed by intensive decomposition and loss of solubility of the polymer. The loss in solubility of the polymer serves as an indication that under the experimental conditions crosslinking is the predominating process.

In all cases the nitrogen content of the polymer was determined after heat treatment and since there was no change in the percentage nitrogen content though the loss in weight was considerable, it may be assumed that in addition to other volatile decomposition products compounds containing nitrogen are also split off.

Table 3 shows the results of elementary analysis of the untreated polymer and of the product after thermal-oxidative treatment at 200° for 4 hr.

TABLE 3. ELEMENTARY COMPOSITION OF PHMAA

Elementary composition	C	H	N	O
Calculated figures	63·72	9·73	12·38	14·16
Analytical figures:				
(a) before heating	61·60	9·70	12·23	16·50
(b) after heating	62·73	9·53	12·14	15·60

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As is seen from Table 3 the elementary composition of PHMAA changes little on heating. The nitrogen and hydrogen contents are almost unchanged and the carbon content is increased as a result of a decrease in oxygen content. This indicates that the decomposition of PHMAA evidently takes place according to a scheme similar to that for PCA where the volatile products are equivalent to the composition of a segment.

(c) *Polyamide fibres.* The polyamide fibres (Anid and Kapron) were subjected to thermal and thermal-oxidative treatment at various temperatures for different times in atmospheres of nitrogen and oxygen. Results of the determination of the viscosity of 0·5% solutions of the fibres in tricresol and also of changes in physicomechanical characteristics after thermal and thermal-oxidative treatment are shown in Table 4 and Fig. 3.

As the data of Table 4 and Fig. 3 show, heat treatment of both the polymers and the derived fibres causes an increase in the viscosity of 0·5% solutions in tricresol and thermal oxidation causes a decrease. It may be assumed that under the experimental conditions the predominant process on heat treatment is crosslinking, and on thermal oxidation, degradation. Further heating of the polyamide fibres at temperatures above 200° gives insoluble products and this occurs earlier for Kapron than for Anid (Table 4), evidently as a result of the presence of monomer which enhances the predominance of the crosslinking process. Table 4 shows that Anid fibre is more stable to the action of high temperatures than is Kapron fibre. The lower resistance of Kapron to high temperatures should probably also be related to the presence of monomer in the fibre.

On the basis of previously known data from the literature and of our experimental results some hypothetical views may be expressed on the machanism of the degradation of polyamides which is brought about by the rupture of weak C–N bonds with the formation of free radicals of the type

$$-NH-(CH_2)_x-\overset{\overset{O}{\|}}{C}-NH-(CH_2)_x-CO- \longrightarrow$$

$$\longrightarrow -NH-(CH_2)_x-CO\cdot + \cdot NH-(CH_2)_2-CO\cdot .$$

The radical formed abstracts the most labile hydrogen atom from the polyamide molecule, regenerating an active centre R′:

$$-NH(CH_2)_xCO\cdot + \cdot NH(CH_2)_2CO\cdot \longrightarrow NH(CH_2)_xCOOH + \cdot CO(CH_2)_xN\cdot .$$

It is probable that other reactions are involved in the development of the process, with recombination of radicals with the formation of double bonds, for example

$$-NH(CH_2)_xCO\cdot \longrightarrow NH-CH=CH-CH=CH-(CH_2)_x-CH_3 + CO + H_2O$$

for which there is some support in the change in colour of the polyamide, normally brought about by the formation of conjugated double bonds. Obviously this

TABLE 4. CHANGES IN PROPERTIES OF POLYAMIDE FIBRES AFTER THERMAL AND THERMAL-OXIDATIVE TREATMENT

Temperature (°C)	Anid								Kapron							
	In nitrogen				In oxygen				In nitrogen				In oxygen			
		Physico-mechanical characteristics				Physico-mechanical characteristics				Physico-mechanical characteristics				Physico-mechanical characteristics		
	Viscosity (η_{sp})	Elongation at break (km)	Elongation (%)	Number of double flexings	Viscosity (η_{sp})	Elongation at break (km)	Elongation (%)	Number of double flexings	Viscosity (η_{sp})	Elongation at break (km)	Elongation (%)	Number of double flexings	Viscosity (η_{sp})	Elongation at break (km)	Elongation (%)	Number of double flexings
Original	0·576	59·3	16·8	2189	0·576	59·3	16·8	2189	0·729	55·3	17·3	1402	0·729	55·3	17·3	1406
160	0·578	59·6	19·5	2157	0·547	48·5	15·9	1235	0·734	51·2	21·2	—	0·479	29·6	13·2	829
170	0·582	59·8	23	2131	0·416	35·8	15·1	879	0·805	50·4	24·3	—	—	23·0	10·2	298
180	0·621	58·9	23·2	2142	0·382	28·9	14·3	523	0·867	48·2	24·4	—	0·274	19·0	9·7	—
200	0·692	57·3	23·2	2322	0·273	18·8	9·0	12	not observed	43·3	25·0	—	not observed	3·5	3·9	—
210	—	53·4	22·7	2440	0·265	14·6	8·4	10	—	—	—	—				
220	—	51·3	22·0	2420	0·155	5·02	2·1	9·0								

recombination can also be accomplished in intermolecular reactions, evidence of which is given by the loss in solubility of the polymer as a result of cross-linking.

From the data presented on the changes in properties of different polymers under the action of heat in an inert atmosphere and in oxygen the general conclusion applicable to all polymers investigated can be drawn, that substantial changes in the chemical and physicomechanical properties of polymers result from oxidation processes and heat initiates these processes. On the basis of this conclusion a more rational approach to a solution of the problem of stabilization of polymers and synthetic fibres is possible.

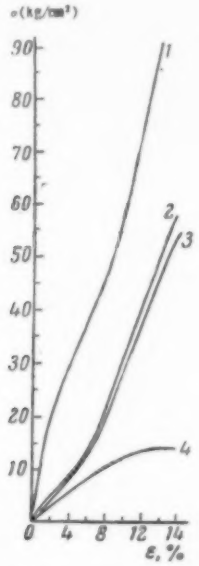

FIG. 4. Mechanical properties of Anid fibre (commercial sample): (1) at −80°; (2) at 20°; (3) at 100°; (4) at 200°.

A separate communication will be made on some approaches to this problem. The importance of the physical manifestations of ageing of polyamide fibres during use has already been pointed out above.

In this connexion the thermomechanical properties of polyamide fibres over a wide range of temperatures have been studied, both in the original state and after subjection to the prolonged action of high temperatures under different conditions.

Figures 4 and 6 show stress-strain curves of Anid and Kapron fibres plotted by means of a Polyani apparatus for test temperatures from −80° to 200°. It is seen from the curves that these fibres are not heat stable and over the temperature range from − 80° to 200° their mechanical properties change considerably with a marked increase in rigidity as shown by an increase in initial

modulus and tensile strength at low temperatures and considerable softening and increase in elastic properties at temperatures close to the melting point of the crystalline phase.

These phenomena of unusual thermal amorphization of polyamide fibres are shown particularly clearly when they are given a preliminary heat treatment in an inert atmosphere (nitrogen) at temperatures close to the melting point of the crystalline phase, without changing the phase state.

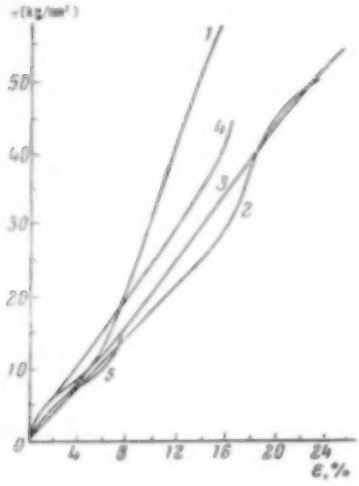

FIG. 5. Mechanical properties of Anid fibre subjected to thermal and thermal-oxidative treatment. Temperature of test, 20°. (1) Original sample; (2) heated in a current of nitrogen at 170°; (3) the same at 210°; (4) heated in air at 170°; (5) the same at 210°.

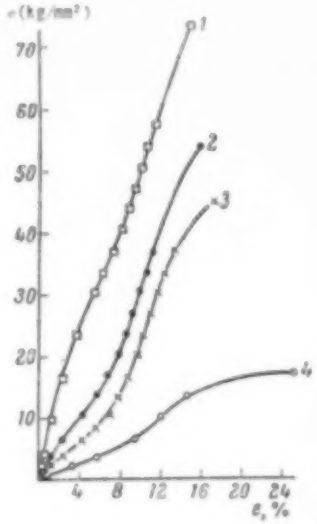

FIG. 6. Mechanical properties of Kapron fibre (commercial sample): (1) at −80°; (2) at 20°; (3) at 100°; (4) at 200°.

Figures 5 and 7 show stress–strain curves of Anid and Kapron fibres after preliminary heating at various temperatures in atmospheres of nitrogen and air, from which it is clearly seen that heating in an inert atmosphere leads to a stable rise in the elongation at break of the fibres and the initial tensile strength is almost completely maintained, whereas heating in air causes an irreversible loss in tensile strength. In so far as this process is to a considerable extent reversible in the time and temperature scale of the experiment, and consequently cannot be connected with irreversible chemical changes in the polymer, the variation in mechanical properties at these experimental temperatures and times is a result of structural transformations in the polymer, characterized by relaxation processes which, in their effects and possibly also in their nature, are similar to thermal amorphization at temperatures close to the melting point of the crystallites and to the rubber-glass transition phenomenon at temperatures below that at which elastic properties appear in crystalline polymers.

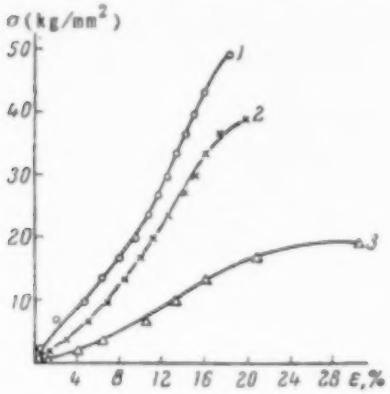

FIG. 7. Mechanical properties of Kapron fibre heated in air for 8 hr at 150°; (1) test carried out at 20°; (2) at 100°; (3) at 200°.

Now that the structural picture of polymers has been clearly separated [14, 15] into parts connected with molecular (primary) structure which is related to the phase state of the polymer and is strongly temperature dependent, and supermolecular (secondary) structure, controlled evidently not by thermodynamic but by kinetic factors which are therefore able to manifest themselves over a wide range of temperatures, the observed, constant, marked change in the elastic properties of polyamide fibres on heating and cooling can be explained by transformations of the secondary structure.

These structural changes are possible as a result of reorientation of the disposition of the crystalline regions or of changes in shape of the secondary fibrillar structures, which under conditions of a high degree of orientation of both types of structural element can lead to non-equilibrium, but long maintained effects of change in mechanical properties.

Further investigations are necessary for a definitive explanation of this unusual thermal amorphization of crystalline structures but whatever their outcome it must be assumed that the mechanical properties of orientated, crystalline polymers are determined not by the phase state but evidently by the secondary, supermolecular structure.

The phenomenon of stable thermal amorphization of libres, observed in this work, must be a general, characteristic property of all crystalline, polymer fibres of high orientation.

CONCLUSIONS

(1) An investigation has been made of thermal and thermal-oxidative treatment of polycapramide, polyhexamethyleneadipamide and the fibres derived from these.

(2) It is shown that substantial changes in the chemical and physicomechanical properties of the polymers and fibres are related to oxidative processes that are accelerated at high temperatures.

(3) An investigation has been made of the variation in thermomechanical properties of polyamide fibres under various conditions over a wide range of temperatures.

(4) An unusual thermal amorphization of the crystalline, polymer fibres has been observed, that results in a maintained increase in the elastic properties of the fibre without any change in phase.

(5) A hypothetical explanation of this phenomenon is given, from the point of view of structural transformations taking place in the molecular and supermolecular structures of the orientated fibres.

Translated by E. O. PHILLIPS

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INVESTIGATION OF DIELECTRIC LOSS AND POLARIZATION IN STEREOREGULAR POLYMETHYLMETHACRYLATE*

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STEREOREGULAR polymers in a number of cases differ markedly in physical properties from atactic polymers. For example the difference in tendency to crystallize and in density, the shift in glass temperature toward lower (isotactic polymethylmethacrylate) or higher temperatures (syndiotactic polymethylmethacrylate etc [1, 2]) are connected with the specific features of their structures. The difference in glass temperature indicates that the stereoregularity of the macromolecules can be ascertained from the relaxation properties of the polymer.

The molecular relaxation of polymers can be investigated by the dielectric method, this method being applicable not only to polar, but also to nonpolar polymers because the latter almost always carry a certain quantity of combined polar groups.

The present work is concerned with a study of the relaxation properties of isotactic and syndiotactic polymethylmethacrylate (PMMA), obtained with organolithium catalysts [1] in A. A. Korotkov's laboratory at the Institute of Macromolecular Compounds.

METHOD

All the samples of stereoregular polymethylmethacrylate were precipitated by methanol from benzene solution, thus guaranteeing complete absence of crystallinity which was confirmed by X-ray diffraction examination [2].

For dielectric measurements, films were prepared by evaporation of benzene solutions on metal plates. For the remaining measurements the method of preparation of the samples was the same as that described previously [3].

The density of the polymers investigated was determined on a hydrostatic balance and the refractive index by means of an Abbe refractometer on films of thickness of the order of 100 μ.

The variation in $\tan\delta$ and dielectric constant ε' was followed over the temperature range from $-160°$ to $140°$ at frequencies from 20 c/s to 100 kc/s. The dielectric measurements were carried out with the apparatus described previously [3].

* Vysokomol. soedin. **2**: No. 4, 619–625, 1960.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of tanδ for isotactic [1], syndiotactic [2] and atactic PMMA, the latter having been obtained by radical polymerization with benzoyl peroxide. Here also a curve of tan$\delta = \Phi(t°)$ is given for a sample of isotactic PMMA which, from the polymerization conditions, has an intermediate degree of regularity [4].

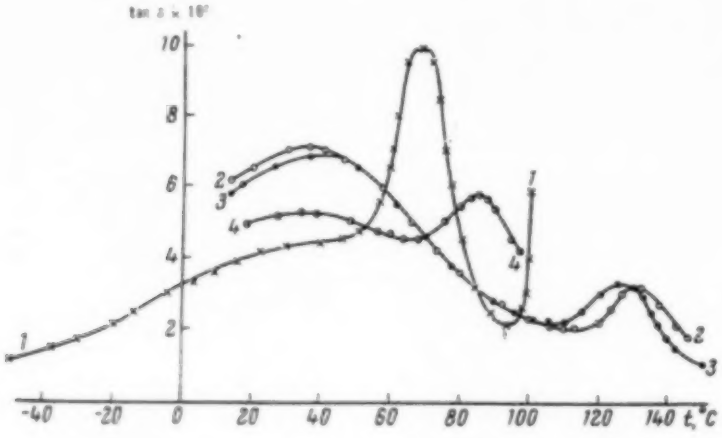

FIG. 1. Temperature dependence of tanδ of PMMA of different stereostructure at a frequency of 28 c/s: (1) isotactic PMMA; (2) syndiotactic; (3) atactic; (4) PMMA of intermediate degree of isotacticity.

It is seen from the diagram that the temperature dependence of tanδ due to dipole losses for syndiotactic and atactic PMMA [4] coincide over a wide temperature range. A shift in the region of $\tan\delta_{max}$ due to dipole-elastic* losses of the syndiotactic sample is observed only at high temperature, which is in accord with the increase in the value of T_g, and a small divergence in the low-temperature region due to dipole radical losses. This identity of the relationship tan$\delta = \Phi(t°)$ is maintained also at another frequency of the applied field at 100c/s (we have omitted this graph in order to save space).

It may be considered therefore that the relaxation time of the dipoleradical process corresponding to side chain mobility is the same for the syndiotactic and atactic molecular structures of PMMA. At the same time τ for dipole-elastic losses is higher for the syndiotactic structure, indicating greater hindrance to the movement of chain segments in this case.

The temperature dependence of tanδ for isotactic PMMA has a totally different character. As for the syndiotactic and atactic polymers there are two

*_Translator's Note_: The terms "dipole-radical" and "dipole-elastic" have proved awkward. My first attempt at a paraphrase became cumbersome when repeated frequently. I have finally left in this literal translation in the hope that it will be acceptable.—_Editor_.

regions of $\tan\delta_{max}$ for isotactic PMMA, one of which corresponds to the dipole-elastic process and the second (on the low-temperature side) to the dipole-radical process.

Whereas for atactic PMMA a wide region of dipole-radical losses is characteristic, $\tan\delta_{max}$ of which exceeds that of the dipole-elastic process by a factor of 2, here there is a marked "redistribution" of the maximal values of $\tan\delta$ for both types of losses. As for many other vinyl-type polymers $\tan\delta_{max}$ for isotactic PMMA is considerably higher for dipole elastic than for dipole radical losses (by a factor of approximately 2). The sample with an intermediate degree of isotacticity gives a $\tan\delta=\Phi(t^\circ)$ curve occupying a roughly mean position.

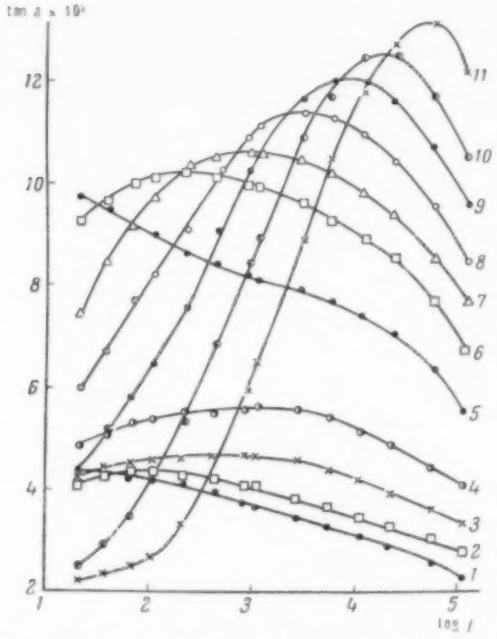

FIG. 2. Frequency dependence of $\tan\delta$ of isotactic PMMA at various temperatures: (1) 24°; (2) 34°; (3) 46°; (4) 56°; (5) 67°; (6) 73°; (7) 78°; (8) 81°; (9) 85°; (10) 89°; (11) 95°.

Measurements at 20c/s were carried out down to −160° and in the low-temperature region $\tan\delta$ fell monotonically with temperature.

Figure 2 shows the frequency dependence of $\tan\delta$ of isotactic PMMA, plotted at various temperatures. The curves at temperatures from 24 to 56° represent the variation of $\tan\delta$ due to dipole-radical losses. At 67°, on the low frequency side the region of dipole-elastic losses is imposed, the effect of which increases with increase in temperature. Comparison of the temperature and frequency dependences of $\tan\delta$ of this sample of PMMA leads to the conclusion that the curves of $\tan\delta=\Phi(f)$ at temperatures of 76° and above represent the dipole-

-elastic process though some distortion is possible due to the superposition of dipole radical losses.

The shape of the frequency dependence of dielectric constant $\varepsilon' = \Phi(f)$, shown in Fig.3, corresponds fully to the variation of tanδ with frequency.

Of particular interest in this case is the function $\log f_m = \Phi(10^3/T)$, calculated from the results of the temperature-frequency investigations (Fig.4) (T is the absolute temperature of the maximum in tanδ at a frequency of f_m). In the temperature region where dipole-elastic and dipole-radical losses can be observed separately at the same frequency the function $\log f_m = \Phi(10^3/T)$ consists of straight-line sections, the slopes of which may be regarded as the temperature coefficients of the relaxation times of the corresponding processes (u).

At higher temperatures, as is seen from the temperature and frequency curves of tanδ (Fig. 1 and 2) progressive superposition of the dipole-radical and dipole-elastic regions is observed. In other words combination of the relaxation processes of pendant side groups and of chain segments takes place. In this case the temperature of the maximum in the dependence of tanδ on temperature or frequency, representing in a certain sense the superposition of dipole-radical and dipole-elastic losses, is related to the frequency f_m in a more complex manner, not included within the framework of the general equation $f_m = f_0 e^{-U/RT}$.

In Fig. 4 this is reflected in the curved section of function $\log f_m = \Phi(10^3/T)$ for the dipole-elastic losses.

Investigations carried out on a number of polymers show that at certain temperatures the relaxation times of the dipole-elastic and dipole-radical processes approach one another and at a temperature above that corresponding to $\tau_{d.e.} = \tau_{d.r.}$ only one relaxation process is observed [5, 6]. The existing experimental material enables the suggestion to be made that this process can be described by a spectrum of relaxation times, the temperature dependence of the most probable value of τ from this spectrum coinciding with the straight-line section of $\log f_m = \Phi(10^3/T)$ for dipole-radical losses. In comparison with atactic PMMA the isotactic sample has a shorter relaxation time of dipole losses of both types (the dotted lines in Fig. 3 and 4 correspond to the dipole-radical process in the atactic polymer).

The apparent activation energy or temperature coefficient of the relaxation time of dipole-radical losses is 24 kcal/mole which almost coincides with the corresponding values for the atactic sample (21 kcal/mole). The corresponding value for the dipole-elastic process as before remains very high at 138 kcal/mole. Thus there is little change in the activation energies of the dipole-radical and dipole elastic processes on passing from the atactic to the isotactic structure of PMMA.

The glass temperature, T_g, at which the relaxation time relating to movement of the chain segments is 1 sec, according to the dielectric measurements is 60°. This figure is in good agreement with the values of T_g reported in the literature, determined by other methods. The temperature at which the relaxa-

tion time that characterizes the mobility of side chains is 1 sec, according to the data of Fig. 4, is $-12°$.

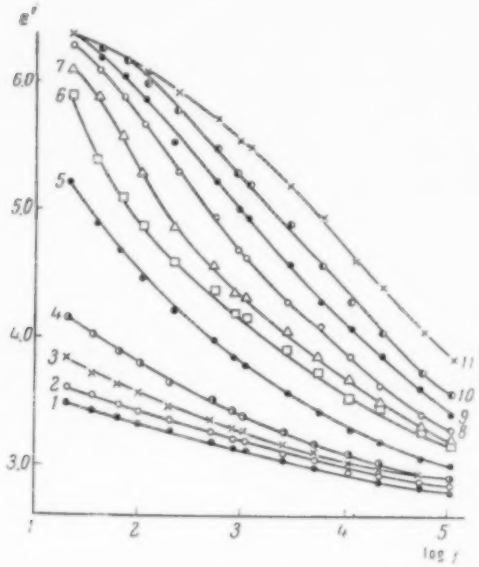

FIG. 3. Frequency dependence of the dielectric constant of PMMA. Temperatures the same as in Fig. 2.

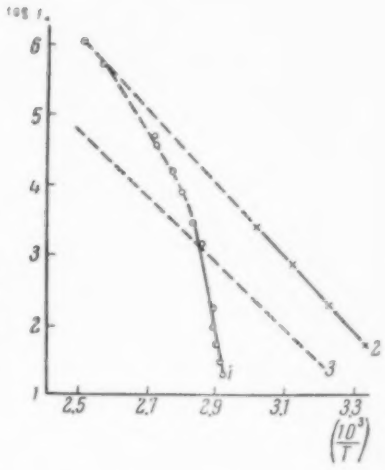

FIG. 4. The relationship $\log fm = \Phi(10^3/T)$ for isotactic PMMA: (1) dipole-elastic losses; (2) dipole-radical losses; (3) dipole radical losses of atactic PMMA.

At the present time there is a very limited method of analysis of dielectric relaxation-time spectra. However we have attempted to estimate the parameter, α, of the distribution of relaxation times, reflecting the spread of the spectrum, by the circle-diagram method [7]. Figure 5 shows the relationship $\alpha = \gamma(t°)$, where α is related to the distribution parameter from the circle diagrams (β) by the well known equation

$$\alpha = (1-\beta)/\left[\sqrt{2}\cos\left\{(1-\beta)\pi/4\right\}\right]$$

The parameter of spread, α, calculated for the dipole-radical relaxation spectra (temperature region from 24° to 56°), increases slowly with temperature. At higher temperatures the calculation relates to the dipole-elastic relaxation spectrum and here the increase in α is steeper. Unfortunately the temperature-frequency range in which the present measurements were carried out does not enable more concrete conclusions to be made about the nature of the variation in spread of the relaxation spectra of both types, both in the region where they co-exist and at higher temperatures where they merge together.

The experimental material presented shows how the isotactic molecular structure affects molecular relaxation in PMMA. From the point of view of study of

structural bonds and polymer properties investigation of the effective dipole moments, calculated from temperature-frequency and static dielectric data, is of great interest.

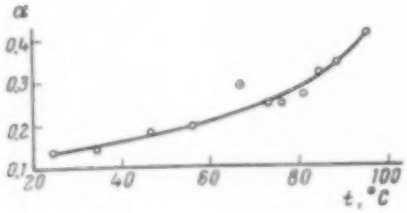

FIG. 5. Dependence of the parameter, α, of the spread of the spectrum of relaxation times, with temperature, for isotactic PMMA.

The statistical theory of Harris and Adler [9] was used for these calculations Details of the calculation have been described previously [10]. The results are shown in Table 1 where the necessary values of density ρ and the square of refractive index (n_D^2) are also given.

TABLE 1. EFFECTIVE DIPOLE MOMENTS OF PMMA DERIVED FROM THE TEMPERATURE-FREQUENCY RELATIONSHIPS OF THE GENERALIZED DIELECTRIC CONSTANT

Temperature (°C)	ρ (g/cm³)	n_D^2	$(\mu\sqrt{g})_{d.r.}$ (debyes)	$(\mu\sqrt{2})_1$ (debyes)	$(\mu\sqrt{2})_{d.r.}$ (debyes)	$(\mu\sqrt{g})_2$ (debyes)	Temperature (°C)	ρ (g/cm³)	n_D^2	$(\mu\sqrt{g})_{d.r.}$ (debyes)	$(\mu\sqrt{2})_1$ (debyes)	$(\mu\sqrt{2})_{d.r.}$ (debyes)	$\mu(\sqrt{g})_2$ (debyes)
24	1·210	2·258	1·1	1·2	—	—	76	1·194	2·234	—	—	1·6	1·9
34	1·207	2·253	1·1	1·3	—	—	81	1·193	2·233	—	—	1·6	1·9
46	1·203	2·247	1·1	1·3	—	—	85	1·193	2·233	—	—	1·5	1·8
56	1·200	2·242	1·2	1·4	—	—	89	1·192	2·231	—	—	1·5	1·8
67	1·197	2·238	1·2	1·5	—	—	95	1·191	2·230	—	—	1·4	1·8

The effective dipole moments $(\mu\sqrt{g})_{d.r.}$ and $(\mu\sqrt{2})$, were calculated from dipole-radical loss data. This means that the magnitude $(\mu\sqrt{g})_{d.r.}$ characterizes molecular structure and molecular interaction that are determined only by movement of side-chain radicals, if the main chain is considered as being immobile. $(\mu\sqrt{g})_{d.r.}$ was calculated from the equilibrium values of the generalized dielectric constants ε_0, and ε_{∞_1}, found from the circle diagrams for dipole-radical losses. It is obvious that ε_0, and ε_{∞_1} are connected only with that part of the static polarization resulting from orientation of dipoles in the pendant side chains with an immobile main chain. The magnitude $(\mu\sqrt{g})$ characterizes the "quasi-statistical" effective dipole moment which includes polarization not only as a result of orientation of polar side groups but also any other type taking

place at a higher rate, for example, deformation polarization or polarization resulting from orientation of dipoles having a shorter relaxation time than the dipole-radical process under examination.

$(\mu\sqrt{g})_{\text{d.e.}}$ and $(\mu\sqrt{g})_2$ can be determined in a similar way but from dipole-elastic loss data. It should be noted that $(\mu\sqrt{g})_2$, calculated from the temperature-frequency relationships of ε' and ε'' should coincide with the value of the statistical effective dipole moment, calculated from the statistical value of the dielectric constant ε_0, and this is confirmed within the limits of error in Table 2.

TABLE 2. EFFECTIVE DIPOLE MOMENTS OF ISOTACTIC PMMA CALCULATED FROM THE STATISTICAL DIELECTRIC CONSTANT

t, °C	ρ(g/cm³)	n_D^2	ε_0	$\mu\sqrt{g}$, D
110	1·188	2·225	5·78	1·79
130	1·184	2·219	5·44	1·75

The method of treatment of the experimental data by means of circle diagrams over a wide temperature range is not free from a certain degree of arbitrariness, which limits the accuracy of the calculation of effective dipole moments. Calculation from the statistical dielectric constants is considerably more accurate but this is possible only over a very narrow temperature range. We have therefore refrained from making a more detailed analysis of the temperature dependence of effective dipole moments on the basis of the data presented.

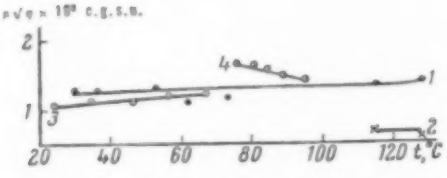

FIG. 6. Variation of effective dipole moments with temperature: (1,2) $(\mu\sqrt{g})_{\text{d.r.}}$ and $(\mu\sqrt{g})_{\text{d.e.}}$ respectively, for atactic PMMA; (3,4) the same for isotactic PMMA.

A comparison of the results obtained for isotactic and atactic PMMA merits attention [11]. For convenience of comparison the values of $(\mu\sqrt{g})_{\text{d.r.}}$ and $(\mu\sqrt{g})_{\text{d.e.}}$ for PMMA of both structures are shown in Fig. 6. It is seen from the diagram that the effective dipole moments characterizing the dipole-radical process are somewhat higher for the atactic than for the isotactic polymer. There is also a corresponding high value of $\tan\delta_{\max}$ for dipole-radical losses of the atactic polymer at almost the same values of the parameter of the spread

of the relaxation-time spectrum A striking agreement between the ratios of $(\mu\sqrt{g})_{\text{d. e.}}$ and $\tan\delta_{\max}$ for dipole-elastic losses of both types of PMMA is observed. For the isotactic polymer both these values are 3 times greater than the corresponding values for the atactic material. Hence the redistribution of the maximal values of $\tan\delta$ for dipole-elastic and dipole-radical losses that takes place on passing to the isotactic structure finds an explanation in a parallel change in the effective dipole moments.

Values of $\mu\sqrt{g}$ found from the statistical dielectric constants of the polymers of both types in the condensed state do not differ substantially [12]. Moreover, measurements carried out in our laboratory, by our colleague L. L. Burshtein, of the effective dipole moments of the polymer in solution at infinite dilution also showed no difference within the limits of error ($\pm 0{\cdot}03\,D$). Consequently intramolecular correlation of the dipoles prevailing in the polymer in the high-elastic state [12] does not depend to any notable extent on the regularity of chain structure.

CONCLUSIONS

(1) A comparison of the temperature-frequency relationships of $\tan\delta$ for atactic and syndiotactic PMMA has shown that this difference in regularity of structure has no substantial effect on the nature of molecular relaxation in this polymer. An increase only in the relaxation time of dipole-elastic losses in the syndiotactic sample was obserwed.

(2) Dielectric relaxation in isotactic PMMA is totally different. $\text{Tan}\delta_{\max}$ of dipole-elastic losses was greater than that of the atactic sample by a factor of more than 3 but the corresponding figure for dipole-radical losses on the other hand was somewhat lower. As a result of such redistribution of the values of $\tan\delta_{\max}$ in isotactic PMMA the relationship $\tan\delta = \Phi(t^\circ)$ acquired the form typical of polymers of the vinyl series, where $\tan\delta_{\max}$ for dipole-elastic losses is very considerably higher than $\tan\delta_{\max}$ for dipole-radical losses. At the same time the relaxation times of losses of both types were lower. Hence the specific effect of the CH_3 group in the α-position in the PMMA molecule is considerably lower in the isotactic material. The nature of the temperature-frequency relationships of $\tan\delta$ in the case of PMMA can serve qualitatively as a criterion of the presence of sections of the chain having the isotactic structure.

(3) Comparison of the effective dipole moments of isotactic and atactic PMMA, calculated from the temperature dependence of the generalized dielectric constant, gives results in full agreement with the observed variation in $\tan\delta_{\max}$ for losses of both types.

The effective dipole moment calculated from the statistical dielectric constant does not differ from that the atactic sample. This may indicate that the degree of intramolecular correlation of the dipoles is maintained in the polymer in the high-elastic state on passing from the atactic to the isotactic structure

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LETTER TO THE EDITOR: THE CONFORMATION, DIMENSIONS AND DIPOLE MOMENTS OF SYNDIOTACTIC MACROMOLECULES*†

T. M. BIRSHTEIN and O. B. PTITSYN

(*Received* 4 *February* 1960)

ANALYSIS of steric interactions of groups of atoms not connected by valence bonds in syndiotactic macromolecules of the type $(-CH_2-CHR-)_n$ shows that each monomeric unit can have two conformations characterized by the angles of internal rotation $(-\Delta_1, -\Delta_2)$ and $(-120°+\Delta_1', \ -120°+\Delta_2')$, where $0 \leqslant \Delta_1$, Δ_2 and Δ_1', $\Delta_2' \leqslant 30°$. Other conformations would correspond to distances between the pairs of atomic groups that are substantially less than their van der Waals radii. The two conformations have the same energy but consecutive gauche conformations $(-120°+\Delta_1', \ -120°+\Delta_2')$ of neighbouring monomeric units are sterically prohibited, hence the crystalline structure of syndiotactic macromolecules corresponds to the conformation of monomeric units $(-\Delta_1, \ -\Delta_2)$, i.e. the planar trans-structure is easily distorted. Obviously both types of conformation are possible in solution.

By making use of the method of calculation of the mean vector characteristics of macromolecules in solution developed earlier by us [1], based on a rotation-isomer macromolecular model [2], we have calculated the mean square distance between the ends, $\bar{h}^2$, and the mean square dipole moment, $\bar{\mu}^2$, of syndiotactic macromolecules, taking into account the correlation between the conformations of neighbouring monomeric units. The calculation, based on the supposition that the valence angle is tetrahedral and $\Delta_1=\Delta_2=\Delta_1'=\Delta_2'=0$ gives

$$\bar{h}^2 = \frac{4}{3} Nl^2 \frac{p+q}{p-q}\left(\frac{p}{1-q}+\frac{1-q}{p}\right), \tag{1}$$

$$\bar{\mu}^2 = \frac{1}{3} nm_0^2 \frac{1-q}{p}\frac{p+q}{p-q}. \tag{2}$$

* Vysokomol. soedin. **2**: No. 4, 628–629, 1960.

† From an analysis made of steric interactions in syndiotactic macromolecules it follows that in addition to the planar trans-structure of crystalline chains (polyvinylchloride, poly-1, 2-butadiene), in principle a structure formed by the alternation of rotation isomers (0°, 0°) and (−120°, −120°) in neighbouring monomeric units is possible. Such a structure, consisting of a spiral with a period of four monomeric units and one turn (equal to 7·3 Å) was in fact established recently by Natta for syndiotactic polypropylene (G. Natta, Makromol. Chem. 35: 94, 1960) (*Note added in proof*).

Here $n=N/2$ is the degree of polymerization, l the length of the unit, m_0 the dipole moment of the monomeric unit, $p=[(1-g_{22})^2/4+g_{12}g_{21}]^{1/2}$; $q=(1-g_{22})/2$, $g_{\alpha\beta}=\exp(-U_{\alpha\beta}/RT)$, $U_{\alpha\beta}$ is the energy of a pair of monomers in the α and β conformations and $\alpha,\beta=1,2$ where 1 corresponds to the (0,0) conformation and 2 is the (-120^0, -120°) conformation. U_{11} was taken for the beginning of the calculation).

From an analysis of steric interactions $g_{12}=g_{21}\simeq 1$ and $g_{22}=0$, i.e. $p=\sqrt{5}/2$ and $q=1/2$. Substituting these values in equations (1) and (2) we obtain $(\bar{h}^2/2Nl^2)^{1/2}=2{\cdot}2$ and $(\mu^2/nm_0^2)^{1/2}=0{\cdot}65$, which is very close to the experimental results (2·3 [3,4] and 0·65 [5], respectively) for atactic polystyrene and poly-*p*-chlorostyrene, which evidently have structures close to the syndiotactic. It is obvious that if there were any significant deviation of g_{12} and g_{21} from 1 and g_{22} from 0 agreement with experiment would not be obtained. The assumption that U_{12} and U_{21} are small and equal and that U_{22} is very large also agrees with experimental data on the temperature dependence of the intrinsic viscosity of atactic polystyrene in various Θ-solvents of similar chemical structure [6,7].

On the basis of the above the conclusion may be drawn that syndiotactic macromolecules consist of segments of planar trans chains containing on the average $\nu=1+(p-q)^{-1}\simeq 3$ monomeric units and of separate monomeric units in the gauche conformation. It should be noted that this is the minimal assessment of the length of the regular section because taking account of the twisting vibration can only increase it.

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FLOW BIREFRINGENCE OF POLY-PARA-TERT-BUTYLPHENYLMETHACRYLATE—II. THE REGION OF HIGH VELOCITY GRADIENTS*

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1. INTRODUCTION

IN a recent communication [1] an investigation of the dynamo-optical properties of solutions of poly-*p*-tert-butylphenylmethacrylate (PPTBPMA) in the region of low shear stresses was described.

The results obtained were in good agreement with the theory [2] which considers the observed birefringence as the sum of two effects—the intrinsic (segmental) anisotropy of the macromolecules and the shape effect.

The segmental anisotropy of PPTBPMA was found to be large and negative in sign. The difference between the main polarizabilities of the segment $\alpha_1-\alpha_2 = -92\times10^{25}\text{cm}^3$. Such optical properties of the molecular chain are in full accord with its structure, i.e. with the presence of large, anisotropic side groups [3, 4].

At the same time properties of the PPTBPMA molecule were discovered that differ markedly from the corresponding properties of the polymers studied previously (polystyrene, polymethylmethacrylate). Separation of the shape effect from the effect of segmental anisotropy enabled the degree of geometric asymmetry of the molecular cluster to be determined and this was found to be considerably greater than that of polystyrene and polymethylmethacrylate [5]. This fact can be regarded as a manifestation of lower thermodynamic flexibility (degree of coiling) of the polymer chains and may be ascribed to the effect of interaction of its heavy, ester side groups.

In this connexion the problem arises of the effect of this interaction on the kinetic flexibility of the polymer chain also, i.e. on the possibility of its deformation under the action of external forces.

In principle flow birefringence enables this problem to be investigated, at least for polymers, with molecules which show negative segmental anisotropy. In such cases, in solutions of flexible polymer chain (polystyrene) an inversion in sign of the birefringence is observed at sufficiently high shear stresses [6], as a result of deformation (uncoiling) of the molecular clusters under the action of viscous-flow forces.

* Vysokomol. soedin. **2**: No. 5, 646–657, 1960.

The theory of this phenomenon, developed for a model of Gaussian, ideally flexible chains (without internal viscosity) [7, 8], is in satisfactory quantitative agreement with experiment for the case of high-molecular polystyrene, where this effect was first observed [6].

The PPTBPMA molecule has a negative segmental anisotropy. Hence with the assumption that it possesses sufficient flexibility, with a suitable choice of solvent it might be expected that solutions of PPTBPMA would exhibit the phenomenon of reversal of sign of flow birefringence at sufficiently high shear stress for deformation of the chains and mutual compensation of the positive shape effect and the negative effect of intrinsic anisotropy.

The present work is devoted to an examination of this phenomenon in a number of fractions of PPTBPMA in carbon tetrachloride.

2. METHOD

The PPTBPMA fractions studied in the first communication [1], in the region of low velocity gradients, served as test samples for this investigation.

The molecular weight M of fractions No. 1, 2 and 3 was determined by light-scattering in acetone solution, and for fractions No. 4, 5, 6 and 7 it was calculated from the intrinsic viscosity $[\eta]_A$ in acetone solution by means of the equation [9]

$$[\eta]_A = 5{\cdot}75 \times 10^{-5} M^{0{\cdot}68} \tag{1}$$

These molecular weights are indicated in the second column of the table (the numbers of the fractions do not correspond with the numbers in reference [1]).

In addition the intrinsic viscosity $[\eta]$ of all the fractions was determined in carbon tetrachloride under conditions of zero shear stress by the method described in another communication [10]. These values of $[\eta]$ are given in the third column of Table. 1.

Measurement of the flow birefringence Δ_n and the angle of orientation was carried out by means of the apparatus used and described in Part I [1]. The values of the intrinsic birefringence (dynamo-optical constants) $[n]$ of the fractions in carbon tetrachloride were determined by the method described in Part I.

$$[n] = \lim_{\substack{g \to 0 \\ c \to 0}} \left(\frac{\Delta n}{g \eta_0 c} \right) \tag{2}$$

where g is the velocity gradient, c the concentration of the solution and η_0 the viscosity of the solvent.

The values found for $[n]$ are given in the fourth column of Table 1.

3. DEPENDENCE OF THE BIREFRINGENCE OF THE SOLUTIONS ON THE VELOCITY GRADIENT

Figure 1 a–g shows the dependence of Δ_n on the velocity gradient g for all the fractions, in solutions of various concentrations.

For the fraction of lowest molecular weight (fraction No. 7) the birefringence is negative in all regions of velocity gradient, in conformity with the low value

TABLE I. CHARACTERISTICS OF FRACTIONS OF POLY-*p*-TERT-BUTYLPHENYL METHACRYLATE

Fraction No.	$M \times 10^{-6}$	$[n]$, $\frac{100\ \text{cm}^3}{g}$	$[n] \times 10^3$	g_0	β_0	$\Theta_f^0 \times 10^{25}$ Gaussian chain	$[n]_f \times 10^8$, Experimental	$\bar{\Theta}_f \times 10^{25}$	p
1	13·2	10·5	82	5500	29·5	33	160	95	3·4
2	7·4	6·4	43	8500	15·6	31	90	88	3·4
3	6·0	5·3	31·6	8600	10·6	30	71	83	3·4
4	2·2	2·4	12·2	22,700	4·6	24	30	78	3·6
5	1·67	1·9	5·6	33,000	4·0	23	20	64	3·3
6	0·57	1·1	0·7	—	—	13·7	8·8	50	3·8
7	0·20	0·48	−0·7	—	—	11·0	2·8	36·9	3·6

of the positive shape effect $[n]_f$ for this fraction (the value of $[n]_f$ for this polymer-solvent system is proportional to the molecular weight M (see for example equation (12)). For the sixth fraction the effect is also negative at the higher concentrations but becomes positive as $c \to 0$ in conformity with the concentration dependence of shape birefringence [11].

In all the high-molecular fractions (Nos. 1—5) the birefringence, Δ_n, is positive in the region of low velocity gradients, g, and increases with increase in g (the shape effect is predominant). The curve of $\Delta n = f(g)$ for each solution reaches a maximum then falls and crosses into the region of negative values of Δn (where the effect of segmental anisotropy is predominant). The point at which the curve intersects the abscissa (inversion of sign of Δn) corresponds to a lower value of g the higher the concentration of the solution. This is explained by the fact that the shape anisotropy of the macromolecules decreases in increasing concentration (see for example, Fig. 7 in Part I [1]).

The shape of the curves of $\Delta n = f(g)$ for solutions of PPTBPMA in carbon tetrachloride is qualitatively quite similar to that of the corresponding curves for polystyrene in dioxan [6].

The similarity in dynamo-optical properties of PPTBPMA and polystyrene is apparent also in the dependence of the angle of orientation α on the velocity gradient g.

As a qualitative example Fig. 2 shows the course of the relationship $\alpha = \alpha(g)$ for PPTBPMA fraction 2 in carbon tetrachloride.

In the region of values of g corresponding to the change in sign of Δn a "break" occurs in the curves of $\alpha = \alpha(g)$, discovered first in solutions of polystyrene in dioxan [14]. This phenomenon is discussed elsewhere [11].

The observed analogy in the dynamo-optical properties of solutions of PPTBPMA and polystyrene in the region if high velocity gradients is evidently an indication of the similar nature of the molecular mechanism of deformation of the molecular cluster under shear stress in the two cases.

For a quantitative consideration of these results the experimental data must be extrapolated to infinite dilution ($c \to 0$).

For this purpose curves of $(\Delta n/c)_{g=\text{const}} = f(c)$ were plotted for each fraction for a number of selected values $g_1, g_2, g_3 \ldots$ By extrapolation of each of these

curves to $c \to 0$ values of $(\Delta n/c)_{c\to 0}$ were obtained corresponding to the different values of g for the given fraction.

By this means curves of $(\Delta n/c)_{c\to 0}$ were constructed for each fraction. The magnitude of the gradient $g_{\Delta n=0}$, at which inversion of birefringence occurs,

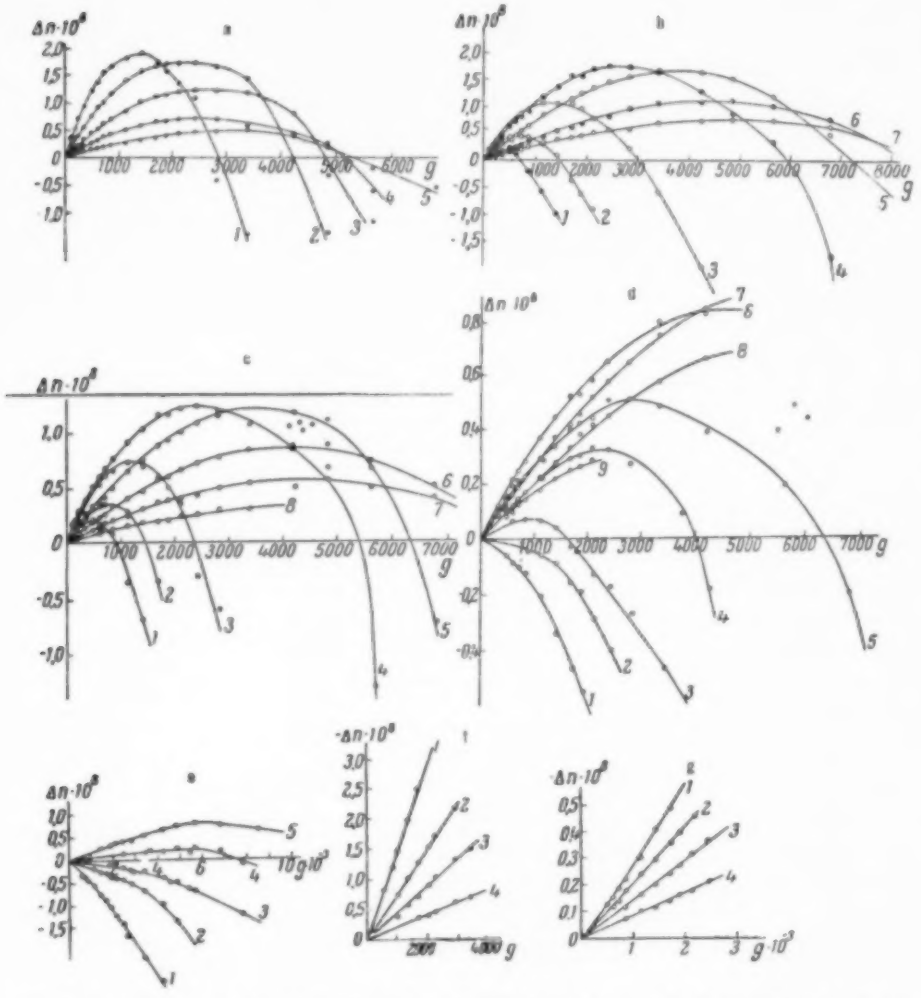

FIG. 1. Dependence of birefringence Δn on the velocity gradient g for solutions of various fractions of PPTBPMA in carbon tetrachloride. (a) 1st fraction (M $13{\cdot}2 \times 10^6$): (1) $c = 0{\cdot}63$; (2) 0·3; (3) 0·16; (4) 0·08; (5) 0·04%. (b) 2nd fraction (M $7{\cdot}4 \times 10^6$): (1) $c = 1{\cdot}73$; (2) 1·46; (3) 1·06; (4) 0·575; (5) 0·285; (6) 0·135; (7) 0·07%. (c) 3rd fraction (M 6×10^6): (1) $c = 1{\cdot}44$; (2) 1·23; (3) 1·05; (4) 0·61; (5) 0·34; (6) 0·16; (7) 0·08; (8) 0·05%. (d) 4th fraction (M $2{\cdot}2 \times 10^6$): (1) $c = 1{\cdot}62$; (2) 1·48; (3) 1·3; (4) 1·25; (5) 0·99; (6) 0·61; (7) 0·4; (8) 0·24; (9) 0·15%. (e) 5th fraction (M $1{\cdot}67 \times 10^6$): (1) $c = 1{\cdot}96$; (2) 1·51; (3) 1·32; (4) 1·07; (5) 0·66%. (f) 6th fraction (M $0{\cdot}57 \times 10^6$): (1) $c = 3{\cdot}4$; (2) 2·5; (3) 1·99; (4) 1·5%. (g) 7th fraction (M $0{\cdot}2 \times 10^6$): (1) $c = 2{\cdot}42$; (2) 2·0; (3) 1·5; (4) 1·0%.

is of particular importance. For each fraction $g_{\Delta n=0}$ is a function of the concentration c, decreasing with an increase in the latter. From the experimental data shown in the curves of Fig. 1 a–e the relationship $g_0=f(c)$ was plotted for each fraction. The graphs obtained for these five fractions are shown in Fig. 3. The

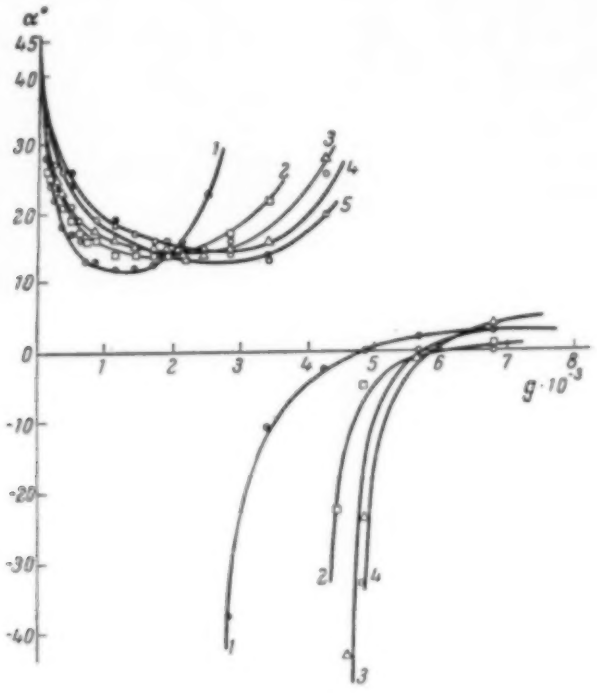

FIG. 2. Dependence of the angle of orientation α on the velocity gradient g for solutions of the 1st fraction ($M=13{\cdot}2\times10^6$) in carbon tetrachloride: (1) $c=0{\cdot}63$; (2) 0·3; (3) 0·16; (4) 0·08; (5) 0·04%.

points lie on straight lines and the points of intersection of these lines and the ordinate correspond to the values $g_0=g_{\Delta n=0}$, the velocity gradient at which inversion of birefringence takes place in an infinitely dilute solution of the given fraction. The values of g_0 found by this means are shown in the fifth column of Table1.

For a comparison of these experimental results with the theoretical data it is convenient to express the values of the birefringence of dilute solutions $(\Delta n/c)_{c\to0}$ as a function of the "normal" parameter β, which is proportional to the shear stress $\eta_0 g$, the molecular weight M and the intrinsic viscosity $[\eta]$ of the fraction.

$$\beta=M[\eta]\eta_0\cdot g/RT \qquad (3)$$

where T is the absolute temperature and R the gas constant.

Figure 4 shows the experimental data for the five high molecular weight fractions in the form of the dependence of the magnitude

$$\lim_{c\to 0}\left(\frac{\Delta n}{c}\right)\times\frac{3n_s}{4\pi}\,\frac{M}{N_A}$$

on the parameter β.

The sixth column of the table shows the experimental values of corresponding to the inversion in sign of the birefringence.

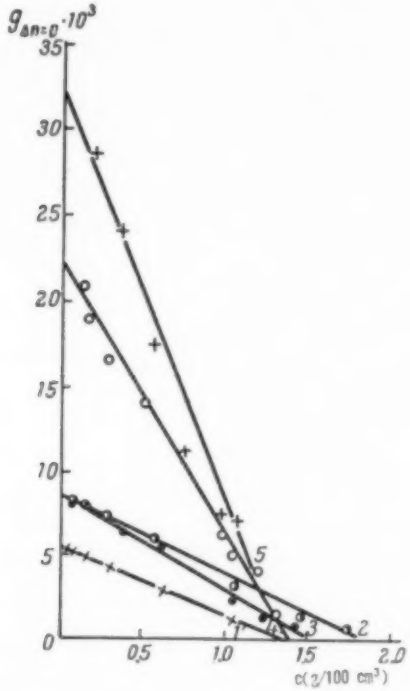

FIG. 3. The concentration dependence of the velocity gradient corresponding to the inversion of birefringence for fractions of PPTBPMA in carbon tetrachloride. The figures on the graphs are the fraction numbers.

4. COMPARISON WITH THE THEORY OF GAUSSIAN CHAINS

It has been shown in a number of papers [5–8, 11] that the observed phenomenon of inversion in sign of birefringence is brought about by the fact that under the action of shear stresses the shape of the molecular cluster in laminar flow becomes asymmetric, and this results in an increase in both the intrinsic (segmental) optical anisotropy of the macromolecule $(\gamma_1-\gamma_2)_e$ and in the optical anisotropy of shape (configurational anisotropy) $(\gamma_1-\gamma_2)_f$. However with an increase in p (the ratio of the semiaxes of the molecular ellipsoid) the increase in $(\gamma_1-\gamma_2)_c$ is more rapid than that of $(\gamma_1-\gamma_2)_f$, hence at certain value of g it is equal to

the absolute value (and opposite in sign), resulting in the disappearance of birefringence (inversion point).

For an optical model of a molecule in the form of a Gaussian cluster in a solution of refractive index n_s Kuhn's theory [12] gives

$$(\gamma_1-\gamma_2)_e=\Theta_e\frac{h^2}{h^2} \tag{4}$$

where h is the distance between the ends of the chain, h^2 is the mean square of this distance and

$$\Theta_e=\left(\frac{n_s^2+2}{3}\right)^2\cdot\frac{3}{5}(\alpha_1-\alpha_2). \tag{5}$$

$\alpha_1-\alpha_2$ is the difference between the polarizabilities of the statistical chain segment.

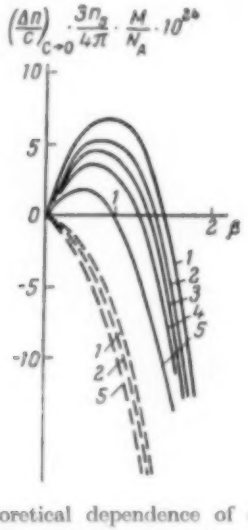

FIG. 4. Curves of the theoretical dependence of $(\Delta n/c)_{c\to 0}\cdot(3n_s/4\pi)\cdot(M/N_A)$ on the parameter β.

The difference in polarization of the molecule $(\gamma_1-\gamma_2)_f$ brought about by the asymmetry of its shape can be expressed in terms of an optical ellipsoid model [2]:

$$(\gamma_1-\gamma_2)_f=\Theta_f^*\cdot(L_2-L_1)=\Theta_f \tag{6}$$

(where (L_2-L_1) is a function of the ratio of the semiaxes of the ellipsoid p).

$$\Theta_f^*=\left(\frac{n_k^2-n_s^2}{4\pi n_s\rho N_A}\right)^2\cdot\frac{M^2}{V}\cdot\frac{1}{(2\pi N_A)^2}\cdot\left(\frac{dn}{dc}\right)^2\cdot\frac{M^2}{V}. \tag{7}$$

Here V is the (optical) volume of the molecular ellipsoid, p the density of the polymer n_k and n_s the refractive indices of the polymer and solvent, dn/dc the polymer-solvent refractive index increment and $N_A=6{\cdot}02\times10^{23}$.

By applying the ellipsoidal optical model to a chain molecule the degree of asymmetry of the ellipsoid p can be expressed in terms of the magnitude of the vector h [7]:

$$p=\left[1+(p_0^{4/3}-1)\frac{h^2}{\bar{h}^2}\right]^{3/4} \tag{7'}$$

Here p_0 is the value of p for a macromolecule in the undeformed state. For a Gaussian cluster $p_0=2$.

The Maxwell effect theory [7] which describes the optical properties of the molecule in terms of equations (4)–(7) and the hydrodynamic properties by means of Kuhn's (dumbell) theory of ideal Gaussian chains [13] leads to the following dependence of Δn on the parameter β:

$$\lim_{c\to 0}\left(\frac{\Delta n}{c}\right)\cdot\frac{3n_s}{4\pi}\,\frac{M}{N_A}=\Theta_e\beta\sqrt{1+\beta^2}+2.28\Theta_f^*\cdot\Phi(\beta), \tag{8}$$

where $\Phi(\beta)$ is a function having the limits $\Phi(\beta)\to\beta$ at $\beta\to 0$ and $\Phi(\beta)\to 4$ at $\beta\to\infty$.

In order to plot the theoretical dependence of the left hand side of equation (8) on the parameter β it is necessary to know the values of Θ_e and Θ_f which characterize the segmental and configurational anisotropy of the molecule respectively.

The segmental anisotropy is independent of molecular weight and is determined from measurements of the dynamo-optical constant of the polymer in a solvent where $n_k-n_s=0$. Such measurements were carried out in bromobenzene (Part I [1] gives $\alpha_1-\alpha_2=-92\times10^{-25}\,\mathrm{cm}^3$).

By substituting this magnitude in (5) and taking $n_s=1{\cdot}462$ (carbon tetrachloride) we obtain $\Theta_e=-105\times10^{-25}\,\mathrm{cm}^3$.

The value of Θ_f^* depends on the ratio M^2/V. For Gaussian clusters the latter can be calculated [5] from the equation

$$\frac{M^2}{V}=\frac{\Phi}{0{\cdot}36}\cdot\frac{M}{[\eta]} \tag{9}$$

where Φ is the Flory constant and is equal to $2{\cdot}1\times10^{23}$.

Taking $n_k-n_s=0{\cdot}1$ for the system PPTBPMA–carbon tetrachloride and making use of the experimental values of M and $[\eta]$ (second and third columns of the table), by means of (7) and (9) we obtain the values of Θ_f^* given in the seventh column of the table.

Figure 4 shows curves (dotted lines), for the 1st, 2nd and 5th fractions of the theoretical relationship

$$\lim_{c\to 0}\left(\frac{\Delta n}{c}\right)\cdot\frac{3n_s}{4\pi}\cdot\frac{M}{N_A}=f(\beta)$$

The values of $f(\beta)$ are calculated from the known values of Θ_e, Θ_f^* and $\Phi(\beta)$ ($\Phi(\beta)$ is tabulated in reference [7]) by means of equation (8), the right hand side of which gives the value of $f(\beta)$.

Direct comparison of the theoretical (Fig. 4) and experimental (Fig. 5) curves shows a marked difference. At all values of the parameter the birefringence remains negative, not changing sign, in contrast to the experimental data.

The reason for this divergence is not difficult to understand, equation (8) having been applied to the region of low velocity gradients $g \to 0$. Then the theory of Gaussian clusters gives for the dynamo-optical constant $[n]$:

$$\lim_{\substack{c\to 0\\ g\to 0}}\left(\frac{\Delta n}{c\eta_0 g}\right)=[n]=[n]_e+[n_f]; \tag{10}$$

$$[n]_f=\frac{4}{3}\pi\frac{1}{n_s}\frac{[\eta]}{kT}\cdot\Theta_e; \tag{11}$$

$$[n]_f=\frac{4}{3}\pi\frac{1}{n_s}\frac{[\eta]}{kT}\cdot 2{\cdot}28\,\Theta_f^*=\frac{4}{3}\pi\frac{1}{n_s}\cdot\frac{1}{kT}\cdot 0{\cdot}397\left(\frac{n_k^2-n_s^2}{\pi\rho N_A n_s}\right)^2\cdot\Phi\cdot M\,. \tag{12}$$

Here $[n]_e$ is that part of the dynamo-optical constant due to the segmental anisotropy of the molecule and $[n]_f$ is the part due to configurational anisotropy.

In order to obtain a positive birefringence in a solution of any of the fractions in the region $\beta \to 0$, $[n]_f$ must be greater than the absolute value $[n]_e$ ($[n]_e$ is negative). Within the framework of the theory of Gaussian clusters (equations 11) and (12)) this condition takes the form

$$28\;\Theta_f^* > |\Theta_e| \tag{13}$$

In fact it can be seen at a glance from the data of column 7 of Table 1 that the condition (13) is not satisfied for any one of the fractions investigated ($\Theta_e = -105\times 10^{-25}\,\mathrm{cm}^3$).

Hence the lack of agreement between the theory of Gaussian clusters and the experimental data is due to the fact that the shape effect in solutions of PPTBPMA is greater than the theory predicts (it should be remembered that for polystyrene the theory gives considerably better results, giving a true assessment of the value of $[n]_f$ (11)).

The experimental value of the shape effect $[n]_f$ at low values of g is determined according to (10) from the relationship

$$[n]_f=[n]-[n]_e \tag{10'}$$

where $[n]$ is the experimental value of the total effect (4th column of the table) and $[n]_e$ is calculated by means of (11) from measurements of $[\eta]$ (3rd column of the table) and substitution of the experimental value $\theta_e = -105\times 10^{-25}\,\mathrm{cm}^3$ in (11).

The values of $[n]_f$ found in this way are given in the 8th column of Table 1.

In the region $\beta \to 0$ the theoretical curves of Fig. 4 can be formally made to coincide with the experimental curves if in place of Θ_f^* in equation (8) the magnitude $\bar{\Theta}_f$ is taken, calculated from the relationship (see equations (11) and (12)

$$\bar{\Theta}_f=\frac{\Theta_e}{2{\cdot}28}\,\frac{[n]_f}{[n]_e} \tag{14}$$

The values of $\bar{\Theta}_f$ are given in the 9th column of the table and the curves of $f(\beta)$ for the 1st–5th fractions, calculated by substituting $\bar{\Theta}_f$ in (8), are shown in Fig.4 (continuous curves). The general shape of these is the same as that of the experimental curves. However the quantitative differences between them in the region of high values of β are very great. However there is no purpose in discussing the cause of this difference because the construction of such "initially coincident" $f(\beta)$ curves is only of illustrative value to emphasize the fact that any theory that explains (though only qualitatively) the dynamo-optical properties of PPTBPMA solutions must take into account the fact that the shape effect plays a greater part than is allowed for in the theory of Gaussian clusters.

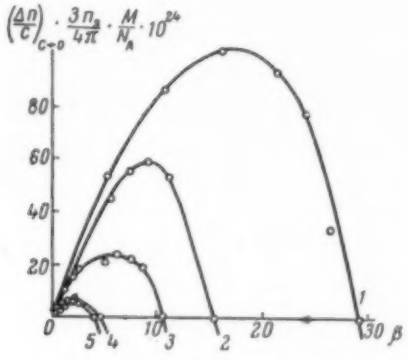

FIG. 5. The experimental dependence of $(\Delta n/c)_{c\to 0} \cdot (3n_s/4\pi) \cdot (M/N_A)$ on the parameter β for PPTBPMA fractions in carbon tetrachloride.

At given values of $n_k^2 - n_s^2$ and M^2/V the magnitude of the shape effect depends on the degree of geometric asymmetry of the molecular cluster p.

In the theory of Gaussian chains, for undeformed macromolecules p takes the value $p_0 = 2$. Taking this value in equations (7) and (6) gives the constant 2·28 in the second term of the right hand side of equation (8). If for the cluster it is taken that $p_0 > 2$ then correspondingly the magnitude of this numerical constant is also increased. However it should be borne in mind that in the region of values of p in which we are interested the magnitude $L_2 - L_1$ of equation (6) is weakly dependent on p. A change in p from $p = 0$ to $p = \infty$ increases $L_2 - L_1$ (and at the same time the numerical constant before $\Phi(\beta)$ in equation (8)) by a factor of only 2.

Meanwhile, for coincidence of the theoretical (Fig. 4) and experimental curves (Fig. 5) in the region $\beta \to 0$ it is necessary to increase this numerical constant by a factor of 3 (compare the value of Θ_f^* and $\bar{\Theta}_f$ in columns 7 and 9 of Table 1) which cannot possibly be done by amendment of only the optical part of the model (i.e. by taking the degree of asymmetry $p_0 > 2$ in equation (6)).

Hence it is not possible, at any value of the degree of asymmetry p_0, to explain the dynamo-optical properties of solutions of PPTBPMA in carbon

tetrachloride (even in the region $g \to 0$) by taking a Gaussian cluster as a model for the hydrodynamic properties of the molecule and an equivalent ellipsoid for the optical properties.

The possibility remains that also the hydrodynamic properties of the polymer molecule studied here may be more correctly described by means of an equivalent ellipsoid model and not by a Gaussian cluster.

5. EQUIVALENT ELLIPSOID MODEL

In the region of low values of g the birefringence can be calculated by means of the theory of rigid ellipsoids [15], as has been shown previously. If an ellipsoid of rotation is taken as a model then the theory gives

$$[n]=\frac{2\pi}{15}\cdot\frac{N_A b}{n_s M\eta_0 D}\cdot(\gamma_1-\gamma_2) \tag{15}$$

where D is the constant of rotational diffusion of particles about a short axis $b=(p^2-1)/(p^2+1)$ and $\gamma_1-\gamma_2$ is the total difference between the two main polarizabilities of the molecule, equal to the sum of the segmental and configurational anisotropy, Θ_e and Θ_f.

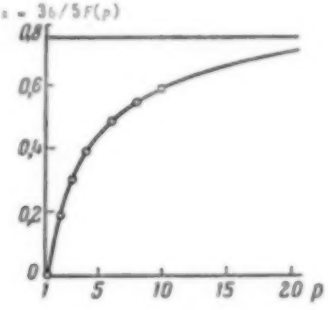

FIG. 6. Graph of function $x=3b/5F(p)$.

For rigid ellipsoidal particles

$$M\eta_0 D=\frac{RT}{6[\eta]}\cdot F(p) \tag{16}$$

where $F(p)$ is a function tabulated by W. Kuhn and H. Kuhn [15].

Substituting (16) in (15) we obtain

$$[n]=[n]_e+[n]_f=\frac{4\pi}{3}\cdot\frac{1}{n_s}\times\frac{[\eta]}{kT}\cdot\frac{3b}{5F(p)}\cdot(\Theta_e+\Theta_f)\,. \tag{17}$$

Equation (17) differs from (11) and (12) by the presence of the factor $x(p)=3b/5F$ which reflects the difference between a rigid ellipsoid and a Gaussian

cluster. The nature of function $x(p)$ is shown graphically in Fig. 6. The configurational anisotropy Θ_f entering into (17) is determined as before from (6) and (7), however equation (9) is not applicable to the ellipsoid model and must be replaced by a combination of equations (16) and (18):

$$D=\frac{kT}{Vf_0\eta_0} \tag{18}$$

where $f_0=f_0(p)$ is a function of the ratio of the axes of the ellipsoid.

By substituting (6) and (7) in (17) and making use of (16) and (18) we obtain for the intrinsic shape birefringence the well known expression [2]:

$$[n]_f=\frac{M}{120\pi\rho^2RT}\cdot\frac{(n_k^2-n_s^2)^2}{n_s^3}[bf_0(L_2-L_1)], \tag{19}$$

which was used also in Part I.

Here, however, it should be borne in mind that V in equation (7) means the volume of the optical equivalent ellipsoid, whereas V in equation (18) is the hydrodynamic volume V_g (the volume of the hydrodynamic equivalent ellipsoid). Equation (19) is derived with the assumption that $V_0=V_g$, If this assumption is not made the factor V_g/V_0 enters into the right hand side of equation (19).

Equation (19) when applied to the experimental results obtained for a number of polymers [5, 7, 18] (with the assumption than $V_g/V_0=1$) gives values of p in the region of 2–2·5, which is in reasonable agreement with theory for the shape of Gaussian clusters. This means that for these polymers the factor $x(p)$ in equation (17), obtained from the shape birefringence $[n]_f$, is close to 0·25 (see Fig. 6).

On the other hand, if the value $x(p)=0{\cdot}5$ is used in the first term of equation (17) the value of the segmental anisotropy Θ_e (and similarly $\alpha_1-\alpha_2$ also), calculated from the experimental value of $[n]_{e1}$ will exceed the value of Θ_e predicted by the strict theory of Gaussian clusters [19] (according to equation (11)), by a factor of 4. Such a large difference obviously results from the inadequacy of the hydrodynamic equivalent ellipsoid model, from which a qualitative description of the hydrodynamic properties of a linear, Gaussian chain can be expected, but there are no grounds for expecting strictly quantitative results in all cases.

It is evident from the above considerations that in application to a polymer molecule equation (17) can be used with accuracy apart from the constant factor, the magnitude of which can be brought into conformity with the experimental data.

Thus by a fourfold increase in the numerical constant in (17) we obtain the expression (20)

$$[n]=\frac{16\pi}{3n_s}\frac{[\eta]}{kT}\cdot x(p)(\Theta_e+\Theta_f), \tag{20}$$

which in the case of Gaussian chains (taking $p=2{\cdot}5$) gives for $[n]_e$ and Θ_e equation (11), which corresponds to the experimental data and strictly to theory [19].

For the shape effect equation (20) in combination with (6), (7), (16) and (18) gives

$$[n]_f = \frac{M}{30\pi\rho^2 RT} \cdot \frac{(n_k^2-n_s^2)^2}{n^3}[bf_0(L_2-L_1)]\frac{V_g}{V_0}. \qquad (21)$$

In order that equation (21) in the case of Gaussian clusters (polystyrene [5], polymethylmethacrylate [17], polybutylmethacrylate [18]) should give reasonable values of $p \approx 2{\cdot}5$ it is necessary to put $V_0 \approx 4V_g$ after which it becomes (19). The latter should also be used for calculating p from the experimental values of $[n]_f$.

As was shown previously [1] and as is seen from Table 1 (columns 2, 8 and 10) for PPTBPMA equation (19) gives the value $p=3{\cdot}5$ which indicates that the configuration of the molecules of this polymer deviates considerably from the geometry of Gaussian clusters.

In conformity with this, putting $p=3{\cdot}5$ in equation (20) leads to the expression.

$$\frac{[n]_e}{[\eta]} = \frac{4\pi}{3} \cdot \frac{1}{n_s} \cdot \frac{1{\cdot}4}{kT}\Theta e$$

and the segmental anisotropy of PPTBPMA from the experimental data is $\Theta_e = -75\times10^{-25}\text{cm}^3$, i.e. 40 per cent lower than the value found from the same data according to the theory of Gaussian clusters (equation (11)).

Hence for macromolecules, the properties of which differ from those of Gaussian chains, the segmental anisotropy θ_e depends not only on the ratio $[n]_e/[\eta]$ but also on the asymmetry factor p.

To some extent this fact affects the value found for the difference in the polarizabilities of the segment $\alpha_1-\alpha_2$, but the effect is hindered in so far as expression (5) is true only for Gaussian chains.

Consequently a model of hydrodynamically and optically equivalent ellipsoids enables the dynamo-optical properties of PPTBPMA solutions in the region of low shear stress to be described satisfactorily, i.e. it presents the possibility of determining quantitatively the initial slopes of the curves of Fig.4, relating them to such molecular characteristics as the degree of geometric asymmetry and the segmental anisotropy of the molecular cluster.

For a quantitative explanation of the optical behaviour of solutions in the region of large velocity gradients it is evidently necessary to take into account deformation of the ellipsoidal particles in the field of shear stresses. The optical properties of the particles subjected to deformation can be described within the framework of earlier work, already mentioned [2, 7], whereas their hydrodynamic behaviour in flow (for example, as a function of the ratio of the axes of the ellipsoid) requires further theoretical examination.

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CONCLUSIONS

(1) The flow birefringence of solutions of poly-*p*-tert-butylphenylmethacrylate (PPTBPMA) in carbon tetrachloride has been studied. Seven fractions of molecular weight $M=(0{\cdot}2-13)\times10^6$ were studied in the velocity-gradient range, g, from 100 to 27,000 sec^{-1}.

(2) In the case of five high molecular weight fractions in the region of low values of g the birefringence Δn is positive, it increases with increasing g to a maximum, then decreases with further increase in the rate gradient, passing into the region of negative values. The general shape of the curves of $\Delta n=f(g)$ is qualitatively the same as that of the curves obtained previously for polystyrene in dioxan [6].

(3) The birefringence angle of orientation α for these solutions also depends "anomalously" on the velocity gradient. In the region of value of g corresponding to inversion of the sign of Δn a "break" occurs in the curves of $\alpha=\alpha(g)$, which was also observed previously for polystyrene in dioxan [11].

(4) The observed phenomena can be explained qualitatively in terms of the same molecular mechanism as for polystyrene. They are caused by deformation and changes in the optical anisotropy of the molecular cluster in the field of shear stresses.

(5) A quantitative comparison of the experimental curves of the relationship $\Delta n=f(g)$ with the theoretical results [7] shows that is not possible to explain the dynamo-optical properties of PPTBPMA solutions by taking a Gaussian cluster as a model for the hydrodynamic properties of the molecule and an equivalent ellipsoid for the optical properties, either in the region of low or of large shear stress.

(6) On the other hand a model of hydrodynamically equivalent ellipsoids enables the birefringence to be explained quantitatively in the region of low shear stress, taking into account such molecular parameters as the degree of geometric asymmetry and segmental anisotropy of the molecular cluster. The model of a deformed ellipsoid also provides qualitative agreement with the general shape of the experimental curves in the regions of medium and high shear stress.

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THE PREPARATION AND PROPERTIES OF SOME AROMATIC POLYMERS*

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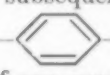
THE investigation of methods of synthesis of linear polyphenyls is of great theoretical and practical interest at the present time. This class of compound, possessing chains of uninterruptured conjugation, would be expected to exhibit the properties of conductors and semiconductors, and also have high thermal stability [1–3]. Up to now there are few papers in the literature devoted to the synthesis and investigation of linear polyphenyls. This can be explained in part by the great difficulties that have confronted the investigators in studying their properties. Polyphenyls have been obtained by the Wurtz-Fittig [4, 5] and Ullmann [6] reactions. Their methyl derivatives have been prepared by the Ullmann reaction [7] and also through the organomagnesium compounds [8]. Recently partially aromatized products from the dehydrogenation of linear polycyclohexadiene-1,3 were obtained, but the dehydrogenation did not go to completion [9]. Perfluoropolyphenyl has been prepared by the Ullmann reaction [10]. All the above methods of preparation are little suited to the synthesis of substituted polyphenyls containing various functional groups. Two of the authors of this paper have for the first time made use of the reduction of bis-diazotized benzidine and benzidine-2,3-dicarboxylic acid by monovalent copper salts, for the synthesis of an homologous series of polyphenyls [11].

If the radical nature of the Sandmeyer reaction as described in the literature [12] is accepted, it becomes evident that on reduction of bis-diazonium ions by Cu^+ ions radicals and biradicals are formed. Polymer of the type of polyphenyl is then formed by subsequent recombination [13]. The presence of diazo radicals of the type of —  —N_2. in addition to hydrocarbon radicals, results in the inclusion of azo groups in the polymer chain.

The mild reaction conditions should lead to a minimum of branching, which is marked in the preparation of polyphenyls by the Ullmann and Wurtz-Fittig reactions, especially the latter. These mild conditions also enable almost any functional group in the starting materials to be preserved unchanged, and a whole series of substituted, linear, aromatic polymers to be prepared.

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The subject of the present work was a study of the conditions for carrying out this reaction and of the properties of the products obtained.

DISCUSSION

The decomposition of bis-diazotized benzidine and benzidine-3,3-dicarboxylic acid was carried out in an ammoniacal solution of monovalent copper both in the presence of air and in an atmosphere of argon. Different orders of mixing the reagents were tried, the copper solution was run in to the diazo solution (subsequently this will be conventionally called the direct order), and the diazo solution to the copper solution (reverse order). The polymers obtained from benzidine are denoted by the figure I and those from benzidine dicarboxylic acid by II.

The results of elementary analysis of the products obtained, shown in Table 1, indicate that in no case was complete elimination of nitrogen achieved. The effect of the carboxyl group in the ortho position to the diazo group leads to considerably more complete elimination of nitrogen. This is quite understandable and agrees with information in the literature [14].

Chlorine evidently forms end groups. This is supported by analyses of various fractions of the polymers. Fractions that are insoluble in benzene and acetone and are therefore of high molecular weight always contain less chlorine than the soluble fractions of the same samples. An example of this distribution of chlorine among the fractions is shown in Table 2.

TABLE 1. ELEMENTARY COMPOSITION OF PRODUCTS

Substance	Order of addition of reagents	Medium	Sample No.	Composition (%)					
				C	H	N	Cl	Total	(by difference)
I	Reverse (D→Cu⁺)	Air	1	80·35	4·35	7·61	3·94	96·26	
				80·40	4·35	7·63	4·15	96·53	
		Argon	2	78·30	4·94	7·77	8·84	99·85	
				78·55	4·91	7·75	8·74	99·95	
	Direct (Cu⁺→ D)	Air	3	79·60	4·29	5·69	10·25	99·83	
				78·58	4·51	5·68	10·06	99·83	
		Argon	4	76·68	4·38	4·86	13·47	99·39	
				76·53	4·21	4·76	13·58	99·08	
II	Reverse (D → Cu⁺)	Air	5	65·85	3·28	2·06	3·54	74·85	25·15
				65·90	3·25	2·27	3·58	75·00	25·00
		Argon	6	64·55	3·80	2·55	4·32	75·22	24·78
				64·80	3·78	2·68	4·25	75·51	24·49
	Direct (Cu⁺→ D)	Air	7	61·65	4·18	3·39	7·28	76·50	23·50
				61·80	4·10	3·28	7·43	76·61	23·39
		Argon	8	60·40	3·97	1·88	10·71	76·96	23·04
				60·30	3·92	1·92	10·82	76·96	23·04

TABLE 2. ELEMENTARY COMPOSITION OF POLYMER FRACTIONS

(For I the composition of the fraction Sample No. 4 from Table 1 is given; for II the composition of the unfractionated polymer is not given)

Substance	Sample	Composition (%)			
		C	H	N	Cl
I	Fraction soluble in benzene	76·50	4·29	2·72	16·55
		76·38	4·07	2·72	16·76
	Fraction insoluble in benzene	78·53	4·68	5·50	10·36
		78·64	4·33	5·50	10·30
II	Fraction soluble in acetone	62·02	4·20	2·44	7·71
		62·15	4·21	2·38	7·75
	Fraction insouble in acetone	62·70	3·63	3·34	6·39
		62·55	3·62	3·34	6·65

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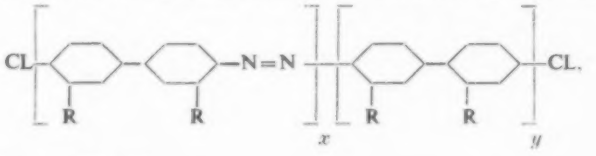
The order of addition clearly affects the chlorine content in the final product. The reverse order, when reduction of the diazonium salt takes place in an alkaline medium in the presence of excess reducing agent, results in the formation of products of high molecular weight. Conducting the process in an atmosphere of argon did not promote an increase in molecular weight or improved elimination of nitrogen, i.e. the intermediate and end products (as is seen from the analytical results) are practically indifferent to the oxygen of the air. It is interesting that under comparable conditions a decrease in chlorine content is accompanied by an increase in nitrogen content. Evidently as the chain lenght increases the elimination of the nitrogen in the conjugated chain is hindered.

The composition of the products may be denoted by the formula



where R is $-H$ or $-COOH$.

The analytical results indicate that on the average for polymer I there is one azo group per 4–6 benzene nuclei and two chlorine atoms per 6–20 benzene nuclei. For polymer II there is one azo group per 6–10 benzene nuclei and two chlorine atoms per 6–15 benzene nuclei.

Potentiometric titration showed that the carboxylic-group content of polymer II (sample No. 5) was 35·0 per cent. The molecular weight of the acetone-insoluble fraction of polymer II was approximately 3000, and that of the ben-

zene-soluble fraction of polymer I was 700 (the elementary compositions of the samples are shown in Table 2). Hence the average number of benzene nuclei in the molecule of the acetone-insoluble fraction of polymer II is 23–24. Correspondingly the samples containing less chlorine must have higher molecular weights.

The intrinsic viscosity of the samples with the lowest chlorine content was ~ 0·1. Fractionation has a very distinct effect on the value of $[\eta]$. For example, sample No. 4 had $[\eta]=0{\cdot}053$, its benzene-soluble fraction, 0·027, and the benzene-insoluble fraction 0·070. The low intrinsic viscosity values also indicate that the molecular weights of these products are relatively low. The dependence of the reduced viscosity on concentration is shown in Fig. 1a, b and c. It is seen from the graphs that the viscosity curves of all the polymer samples follow an anomalous course. Similar anomalous viscosity curves of polyphenyl solutions have been reported previously [6]. The anomalous viscosity can be explained hypothetically by interaction of the rod-shaped polymer molecules which form, at relatively high concentrations, bundles or aggregates which undergo capillary flow. At low concentrations interaction between the molecules is weakened and they dissociate chaotically with a resulting sharp increase in viscosity. The lower anomalous viscosity effect in the samples of polymer II may be connected with movement of the benzene nuclei out of the coplanar position and the large deviation of the molecules of this polymer from the ideal rod shape. In addition, interaction between the carboxyl groups and the solvent must occur in the case of the second polymer.

The heat stability of these materials was assessed by the loss in weight at high temperatures. For polymer I (sample No. 1) the loss in weight in 1·5 hours at 300°C was 3·9 per cent, at 350° for the same time, 17·05 per cent and at 400°, 23 per cent; vigorous decomposition set in at 450°. For various samples of polymer II after 1 hr at 450° the loss in weight varied from 28 to 42 per cent. Analysis showed that the chlorine content of the heated samples was approximately halved.

Curves of the loss in weight of some of the samples with time, shown in Fig. 2a and b, indicate that at each temperature (up to 450°) the loss reaches a limiting value fairly rapidly. The large loss in weight of polymer II is explained by decarboxylation, though there was still 11 per cent of oxygen in the sample after heating, showing that the decarboxylation was incomplete. In all cases the colour of the samples was deeper after heating. All the benzene- or acetone-soluble fractions softened at high temperature and the softening-temperature range for the various samples was from 154 to 275°.

Some additional information on the structure of these polymers is provided by a study of their infrared spectra. The absorption maximum in the 1006 cm^{-1} region for polymer I and at 1002 cm^{-1} for polymer II suggests that there is only para substitution in the aromatic nucleus. The lower intensity of this maximum in the case of polymer II is obviously connected with the presence of the carboxyl groups in position 3. Both polymers have an absorption maximum

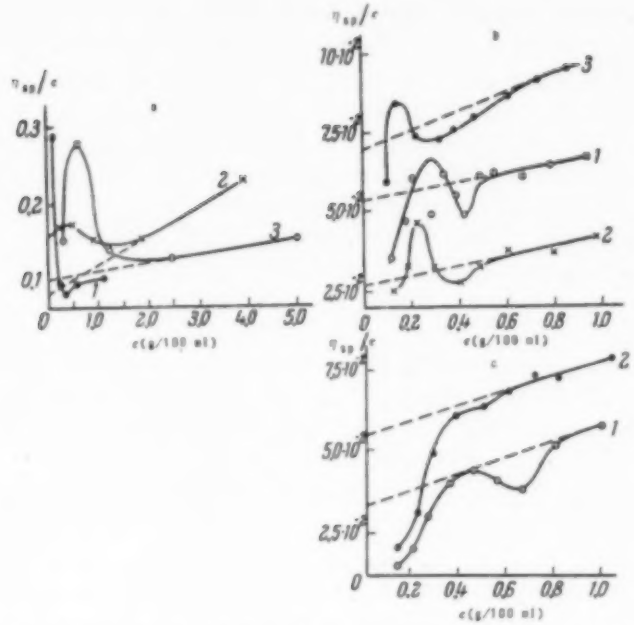


FIG. 1. Dependence of reduced viscosity on concentration (a) (1) Polymer I, sample No. 1, solvent 98% H_2SO_4; (2) polymer II, sample No. 5, solvent 98% H_2SO_4; (3) polymer II, sample No. 5, solvent dimethylformamide; (b) Polymer I, solvent 98% H_2SO_4: (1) sample No. 4, unfractionated; (2) fraction soluble in benzene; (3) fraction insoluble in benzene; (c) Polymer II, solvent 98% H_2SO_4; (1) fraction soluble in acetone; (2) fraction insoluble in acetone.

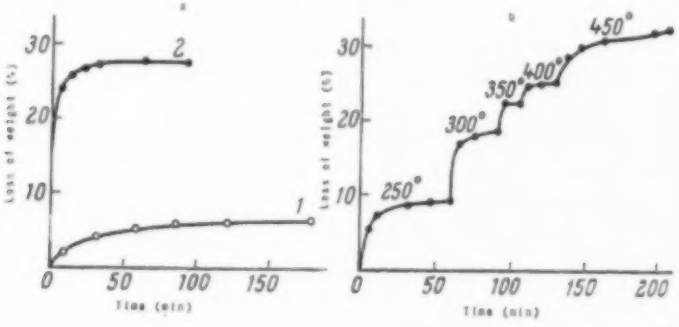


FIG. 2. Loss of weight against time. (a) At constant temperature: (1) polymer I, sample No. 2, fraction soluble in benzene, 300°; (2) polymer II, sample No. 6, fraction insoluble in acetone, 450°: (b) At various temperatures: polymer II, sample No. 6.

in the region of 826 cm^{-1} (I) and 824 cm^{-1} (II), and this is also an indication I of para substitution. The occurence of a maximum at 1380 cm^{-1} for polymer and the absence of a maximum in this region in the case of polymer II suggests

that the bonds between the benzene rings in the first polymer approximate to double bonds, i.e. the product has an approximately quinonoid structure as was found for polyphenyl oligomers [15]. This is also in good agreement with the suggested structures. In polymer II the presence of carboxyl groups hinders conjugation of the π-electron cloud of the benzene rings along the polymer chain as a result of the loss of the coplanar structure. This in turn leads to a lengthening of the C—C bonds between the aromatic rings. Absorption in the 1678 cm^{-1} region in the case of polymer II is due to the carboxyl groups. The remaining maxima have not been identified.

Debye-Scherer diagrams of both polymers (samples No. 1 and 5) show a certain degree of order. A more distinct pattern was given by polymer II.

Electron paramagnetic resonance (EPR) spectra, plotted for various samples of both polymers, showed in all cases a narrow signal of width of the order of 10 oersteds and a *g*-factor of about 2. The intensity of the signal increases with increasing chain lenght. Polymer II gives a wider signal than polymer I, probably because of poorer conjugation. In the case of polymer I the signal is asymmetrical as a result of superposition of the spectra of some type of radical, possibly of peroxide radicals. EPR spectra typical of these materials, have been published by us previously [11]. For both polymers the concentration of unpaired electrons was 10^{18}–10^{19} per gram. After heating at 300–450° the concentration of unpaired electrons increased by 1–2 orders in all cases. The copper salt of polymer II gave a wide (some hundreds of oersteds) asymmetric signal, typical of three-dimensional networks with polar groups. A signal of this type indicates the occurrence of internal-complex formation. In agreement with the EPR spectra measurement of the magnetic susceptibility of the fractions of the two polymers, insoluble in benzene and acetone, showed the presence of paramagnetism with χ of the order of $1\text{–}1{\cdot}5 \times 10^{-6}$ per gram of polymer. More detailed results of the radiospectrometry and of investigations of the magnetic properties and conductivity of these polymers will be published seperately. Study of the EPR spectra and also of the magnetic susceptibility measurements indicates the presence of free radicals in these materials and this provides additional evidence of the radical nature of the reaction.

The fact that in all cases we obtained products of relatively low molecular weight we interpret in the following way. With the growth of the polyphenyl chains the stability of the radical (biradical) increases as a result of the increase in the degree of delocalization of electrons along the conjugated chain and of the amount of quinonoid structure. In the limit a radical is formed that is incapable of further growth under the given reaction conditions. Such inactive biradicals are formed particularly easily when there is an uninterrupted system of conjugated bonds between the unpaired electrons and are known as biradicaloids. In our case the formation of such relatively short biradical blocks is very probable.

These materials are evidently completely unbranched, or there is very little branching. This conclusion is supported both by the infrared spectra and by

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the fact that the chlorine content of the various samples and their fractions, which we consider to form end groups, correlates (at least qualitatively) with the molecular weights of the soluble samples and the viscosities of their solutions. The structure of such rod-like, multinuclear molecules should be close to a quinonoid structure with the possibility of the existence of terminal groups consisting of both chlorine atoms and of unpaired electrons.

Calculation of molecular weight by end-group analysis gives lower values than those found by the isopiestic method, which suggests that there is association in solution. A very much greater degree of association obviously occurs in the solid state. Comparison of the molecular weight figures with the concentration of unpaired electrons in the solid material shows that one unpaired electron goes with tens or hundreds of molecules. This fact, found also in the case of other polymeric, conjugated systems [16], we consider to be directly connected with the possibility of formation of high-molecular, stable macroradicals with delocalized unpaired electrons. These views are supported also by the fact that on heating the benzene-soluble fraction of polymer I with *p*-diethinylbenzene to 200° a black, infusible and insoluble product is formed. We assume that this material is a three-dimensional polymer formed as a result of block-graft copolymerization of the thermally activated biradical with the bifunctional nucleophilic reagent. Such processes in which radicaloids take part might be called radicaloid polymerization processes.

A study of the literature showed that no polyphenyls with more than 34 benzene nuclei have been reported [4,5]. We regard this as indirect support of our views. Only in one case, in the preparation of methyl substituted polyphenyl derivatives from 4,4-di-iodo-3,3-ditolyl [17] by the Ullmann reaction multiple fractionation yielded a narrow fraction with a molecular weight of ~300,000. However this can be explained by partial disturbance of the conjugated system by movement of the benzene rings carrying methyl groups out of the coplanar configuration, and also by the electron-donor properties of the methyl groups. In this case as chain growth proceeds much more active, and not stable, biradicals should be formed. The presence of carboxyl groups in our polymer II also partially disturbs the conjugation along the chain but their electron-acceptor character promotes delocalization of the electrons.

We are very grateful to L. A. Blyumenfel'd, Yu. Sh. Moshkovskii and A. A. Slinkin for investigating the spectra and magnetic properties of the polymers.

EXPERIMENTAL

Ammoniacal solution of monovalent copper. 12·5 g of $CuSO_4 \cdot 5H_2O$ was dissolved in 50 ml. of hot water and 15 ml. of a 25 per cent solution of ammonia was then added. 3·5 g of hydroxylamine hydrochloride in 40 ml of water was added to the resulting hot, dark-blue solution.

Preparation of the polymer from benzidine. A solution of 3·45 g (0·05 mole) sodium nitrite in 18 ml. of distilled water was added to a suspension of 6·45 g (0·025 mole) of benzidine hydrochloride in 50 ml. of distilled water and 8 ml. of hydrochloric

acid of s.g. 1·19 at 0 to +2°, with vigorous stirring. The resulting yellow solution was rapidly filtered from suspended matter into a cooled flask. The ammoniacal solution of monovalent copper salt was then added with vigorous stirring over a period of 15–30 min. to the solution of benzidine bisdiazonium chloride, previously diluted to 300 ml. with water. The reaction temperature was maintained at 0 to +2°. During addition of the reducing agent vigorous evolution of gas occurred with formation of a stable foam and seperation of a precipitate. The reaction mixture was stirred vigorously for an hour at the same temperature and then brought to the boiling point. The polymer was vacuum filtered on a sintered glass filter and washed with water until the wash water became colourless. It was then washed with 10 per cent hydrochloric acid, 10 per cent bicarbonate solution and again with hot water to neutral reaction. The washed material was dried, first in a desiccator over $CaCl_2$ and then *in vacuo* at 100°.

The yield of polymer in various experiments was 4·40–4·62g, i.e. from 115·8 to 121·5 per cent of theoretical yield of polyphenyl. The polymers obtained from these experiments were powders, the colour of which varied from brick-red to brown. Carrying out the preparations in argon or in air, and also changing the order of addition of the reagents, had no significant effect on the colour of the products.

Preparation of the polymer from benzidine-3,3-dicarboxylic acid. Diazotization of the benzidine-3,3-dicarboxylic acid and preparation of the polymer from the bisdiazonium salt was carried out in a similar way to that described above, with the difference that the reaction mixture was brought to boiling point after the addition of 35 ml. of hydrochloric acid of s.g. 1·19. The filtered precipitate of polymer was washed with hot water and 10 per cent hydrochloric acid. The precipitate was broken up on the filter, washed with hot water to negative reaction for Cl ions and dried. The polymers obtained were light-to dark-brown powders. Differences in preparative conditions, as in the previous case, did not affect the colour. With the same molar ratios of starting materials as in the synthesis from benzidine the yield of carboxyl-containing polymers was from 4·65 to 6·31g i.e. from 90·3 to 105·2 per cent of the theoretical yield of polyphenylcarboxylic acid. The nitrogen balance in one of the experiments showed that of the total nitrogen contained in the diazo compound, 87·6 per cent was liberated as free nitrogen and 12·2 per cent entered into the composition of the polymer.

Preparation of the copper salt of the carboxyl-containing polymer. To a previously heated solution of 0·11g of the polymer in pyridine was added a hot solution of 0·08g of crystalline copper acetate in the same solvent. The dark precipitate of the salt was filtered off, washed with pyridine and then with benzene. The washed salt was dried ad 100°; yield 0·13g.

Solubility and fractionation of the polymers. The polymers from benzidine were insoluble in dioxan, chlorobenzene, pseudocumene, tetralin, styrene, dichloroethane, triethylamine, cyclohexanone, ether, tertachloroethane and chloroform. They were partially soluble on heating in benzene, acetone, pyridine, dimethylformamide, nitrobenzene and aniline. The polymers from benzidine-3,3-

dicarboxylic acid were completely soluble in dimethylformamide (without heating), pyridine, dioxan, aniline, cyclohexanone (on heating), and partially soluble in acetone. In all the solvents, with the exception of dimethylformamide, solution was preceded by swelling. All the polymers were soluble in 98 per cent sulphuric acid giving an intense lilac-violet colour. The carboxyl-containing polymers were soluble in aqueous solutions of alkali and sodium bicarbonate.

The polymers from benzidine were extracted with benzene in a Soxhlet apparatus until the extract was colourless. After extraction the solvent was evaporated *in vacuo* and the soluble and insoluble, fractions were dried in the same way as for the original polymer. The content of benzene-soluble fraction in the various samples of polymer varied between 31·2 and 43 per cent. Acetone was used as the solvent for extraction of the carboxyl-containing polymers. The content of acetone-soluble fraction in the various samples varied between 43·5 and 67·1 per cent.

Determination of the molecular weights of the benzene-soluble fraction of polymer I and the acetone-insoluble fraction of polymer II was carried out by the isopiestic method. 1 per cent solutions of the polymers were used. Benzene was taken as solvent in the first case and dimethylformamide in the second. Azobenzene was used as a standard.

Measurement of the viscosity of the polymer solutions was carried out in an Ubbelohde viscometer at $20 \pm 0{\cdot}05^0$. 98 per cent H_2SO_4 and dimethylformamide were used as solvents. The values of $[\eta]$ were determined graphically by extrapolation without taking account of the anomalous rises in the viscosity curves.

The infrared spectra were plotted with an IKS-11 spectrograph. The test samples were pressed into tablets with KBr. Results: polymer I (sample No. 4, fraction insoluble in benzene)—826, 898, 960, 1006, 1036, 1091, 1164, 1189,1231, 1379, 1461, 1579, 1633, 1870 cm^{-1}; polymer II (sample No. 8, fraction insoluble in acetone)—824, 1002, 1036, 1082, 1142, 1220, 1678 cm^{-1}.

The EPR spectra were obtained with a radiospectrometer as designed by Semenov [18], at a wavelength of $\sim 3{\cdot}2$ cm.

Investigation of the heat stability of the polymers in a current of argon was carried out by means of a thermal balance [19] consisting of a crucible furnace containing a U-shaped quartz jacket in which a quartz cup was suspended from a torsion balance by means of a fine platinum wire. The maximum working load of the balance was increased to 5·5 g by means of a counter balance. A filter for the even distribution of inert gas was sealed into the wide arm of the quartz jacket.

CONCLUSIONS

(1). Aromatic polymers with an average molecular weight of up to 3000 have been prepared by reduction of bisdiazo compounds of benzidine and benzidine-3,3-dicarboxylic acid. These products contain a certain proportion of azo groups in the molecule, in addition to the benzene nuclei.

(2) The azo-group content of these products increases with increasing chain length. The presence of carboxyl groups in the ortho position facilitates the elimination of nitrogen during polymer formation.

(3) Investigation of the infrared spectra of the polymers and of the anomaly of the viscosity curves indicates that the benzene nuclei are joined in the para position propably in a quinonoid structure forming rod-like polymer molecules. The mild reaction conditions should facilitate this.

(4) Chlorine atoms and also unpaired electrons evidently occur at the ends of the polymer chains. The presence of unpaired electrons in the final product, at a concentration of 10^{18}–10^{19} per gram of polymer affords confirmation of the radical character of the reaction.

(5) The relatively short chain length of the polymers is evidently connected with the formation of fairly stable biradicals, the reactivity of which is lowered by delocalization of the unpaired electrons along the conjugated chain. The presence of such radicals is confirmed by reaction of these aromatic polymers at high temperatures with *p*-diethinylbenzene with the formation of infusible, insoluble products.

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POLYMERIZATION OF DIALDEHYDES*

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TISHCHENKO [1] has shown that aldehydes form esters under the action of aluminium ethylate in the absence of water

$$2RCHO \rightarrow RCOOCH_2R.$$

Subsequently, however, various investigators have studied the Cannizzaro-Tishchenko reaction in aqueous, aqueous-alcoholic or alcoholic media, and the question of carrying out the Cannizzaro reaction in an anhydrous medium has received little attention in the literature [2].

The object of our work is the application of the Cannizzaro reaction in an anhydrous medium for the polymerization of dialdehydes [3].

It would be expected that, in accordance with the above scheme, dialdehydes in the presence of aluminium alcoholates would form polymers identical in structure with the polyesters formed either by polycondensation of dibasic acids and glycols or of hydroxyacids:

$$\left(-OCH_2-R-CH_2O-\overset{\overset{O}{\|}}{C}-R-\overset{\overset{O}{\|}}{C}-\right)_n; \quad \left(-OCH_2-R-\overset{\overset{O}{\|}}{C}-\right)_n.$$

We have synthesized and polymerized terephthalic, isophthalic and 2,5-dimethylterephthalic aldehydes, and 4,4-diformyldiphenyl. The first three dialdehydes were synthesized by methods reported in the literature and 4,4-diformyldiphenyl was prepared by the Sommle method.

The dialdehydes were polymerized in bulk at temperatures 10–15°C above the melting point of the dialdehyde concerned. The polymers obtained were transparent, yellowish solids reminiscent of polystyrene in external appearance. All the polydialdehydes, with the exception of poly-4,4-diformyldiphenyl were soluble in chloroform, dimethylformamide and cresol. The melting points of the polymers are given in Table 2. The intrinsic viscosity of the products varies over a wide range depending on catalyst concentration, polymerization temperature etc. The molecular weights of separate samples of polyterephthalic aldehyde were within the range of 100,000–120,000 (measured by the light-scattering method).

The rate of polymerization of the dialdehydes depends markedly on catalyst concentration. Table 1 shows that on doubling the concentration of aluminium ethylate the yield of polymer is increased more than 10 times.

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TABLE 1. POLYMERIZATION OF TEREPHTHALIC ALDEHYDE IN THE PRESENCE OF ALUMINIUM ETHYLATE AT 140°C

Concentration of aluminium ethylate (weight %)	Yield of polymer (%)	Polymerization time (hr)
0·6	0·45	65
1·2	8·3	65
3·6	60·5	0·5
3·6	81·0	2
3·6	93·0	4
3·6	99·5	8
3·6	99·9	65

It is also seen from Table 1 that polymerization is practically complete in 4–5 hr at a catalyst concentration of 3·6 per cent. In addition to the ethylate, aluminium isopropylate and phenolate were tried as polymerization catalysts for terephthalic aldehyde. It was found that the isopropylate has no catalytic activity and the activity of the phenolate is very much lower than that of the ethylate. In order to study the structure of polyterephthalic aldehyde it was saponified with alcoholic alkali. The saponification yielded terephthalic acid, *p*-hydroxymethylbenzoic acid and other products that are being investigated. However, it has not yet proved possible to reach a final conclusion on the structure of the dialdehyde polymers.

EXPERIMENTAL

Synthesis of the dialdehydes. The dialdehydes prepared by published methods had the following melting points: terephthalic 115–116° (115–116° [5]); isophthalic 89° (89–90° [6]); 2,5-dimethylterephthalic 101° (102–103° [7]). 4,4-Diformyldiphenyl was prepared by the Sommle method from 4,4-bis (chloromethyl) diphenyl. 2g of 4,4-bis(chloromethyl)diphenyl was dissolved in 10ml of chloroform, the solution obtained was mixed with a solution of 3g of urotropine in 50ml of chloroform and the mixture was refluxed for 5 hr. The precipitated salt was filtered off and dissolved in 60ml of 60 per cent ethanol. The solution was refluxed for 3 hr, after which the ethanol was distilled off. The crystals obtained were dried on a vacuum filter and recrystallized from aqueous alcohol. Yield 1g (67 per cent of theory), m.p. 144–145° (according to the literature, m. p. 145°[8]).
Polymerization of the dialdehydes. 1·5–2g of carefully purified terephthalic aldehyde was placed in an ampoule. All subsequent operations were carried out in an atmosphere of nitrogen, free from oxygen and moisture. The ampoule was pumped out to a residual pressure of 0·5–1 mm and then filled with nitrogen (this operation was repeated twice). A solution of aluminium ethylate in xylene, in the quantity indicated in Table 1, was then fed to the ampoule from a Schlenk

vessel. After addition of the catalyst solution the solvent was completely removed by distillation, the ampoule filled with nitrogen and sealed. Polymerization was carried out in a thermostat maintained within $\pm 1°$. The polymerization yielded a light-yellow, transparent block, soluble in chloroform, dimethylformamide and cresol. After precipitation of the polymer by methanol a white, flocculent powder was obtained. The isophthalic and 2,5-dimethylterephthalic aldehydes and 4,4-diformyldiphenyl were polymerized in a similar way. The polymer of the latter, in contrast to the first three polyaldehydes, was soluble only in hot dimethylformamide; on cooling, poly-4,4-diformyldiphenyl precipitated from solution. The polymerization conditions and melting points of the polymers are given in Table 2.

An attempt was made to polymerize these aldehydes in benzene and toluene at 80°. The polymer began to precipitate from solution immediately after commencement of the polymerization. Investigation showed that the polymer was formed in lower yield and the molecular weight of the polymer was considerably lower than in bulk polymerization.

TABLE 2. CONDITIONS OF POLYMERIZATION OF DIALDEHYDES AND MELTING POINTS OF THE POLYMERS OBTAINED

Dialdehyde	Polymerization temperature (°C)	Concentration of aluminium ethylate (%)	Polymerization time (hr)	Yield of polymer (%)	Melting point of polymer (°C)
Terephthalic	120	3·0	6	99·7	120
Isophthalic	95	3·0	2	91·4	80
2,5-Dimethyl-terephthalic	110	3·6	8	41·0	140
4,4′-Diformyl-diphenyl	180	3·5	0·5	90·0	250

Saponification of polyterephthalic aldehyde. For the study of the structure of polyterephthalic aldehyde 3g of the latter was saponified by alcoholic alkali. 0·95g of terephthalic acid (indentified as its dimethyl ester), 1·50g of *p*-hydroxymethylbenzoic acid and 0·60g of other products were isolated from the saponification products.

CONCLUSIONS

(1) The possibility of preparing polymers from dialdehydes in the presence of aluminium ethylate is shown.

(2) Polymers of terephthalic, isophthalic and 2,5-dimethylterephthalic aldehydes and of 4,4-diformyldiphenyl have been prepared.

(3) The molecular weight of the polymer was found to be 100,000–120,000

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THE HYDRODYNAMIC AVERAGE MOLECULAR WEIGHTS AND CRITERIA OF POLYDISPERSITY OF UNFRACTIONATED POLYMERS*

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The Mark–Kuhn–Houwink (M–K–H) equations express the relationship between intrinsic viscosity [η], the translational friction coefficient f, and molecular weight, in a homologous series of polymers:

$$\left.\begin{aligned}[\eta] &= K_\eta M^a, \\ f &= K_f M^b.\end{aligned}\right\} \tag{1}$$

The parameters a, b, K_η and K_f are characteristic of a given polymer-solvent system and as a rule $a > b$. Only at the Flory Θ-point [1] is $a = b = \frac{1}{2}$.

Equations (1), especially the first of these, are widely used for the rapid determination of molecular weight from the hydrodynamic parameters—[η], the coefficient of diffusion, which is related to f

$$D = \frac{kT}{f} = \frac{kT}{K_f} M^{-b} = K_D M^{-b} \tag{2}$$

and the sedimentation coefficient

$$s = \frac{M(1 - V\rho)}{Nf} = K_s M^{1-b} \tag{3}$$

where k is the Boltzmann constant, T the absolute temperature, N the Avogadro number, V the partial specific volume of the polymer and ρ the density of the solvent. In so far as s and D are concentration dependent (for details see [2]), for analytical purposes equations (2) and (3) should be used only at infinite dilution.

Strictly speaking equations (1) are true only for absolutely monodisperse materials. When applied to a selection of chains of various lengths they give a certain average molecular weight which is usually lower than the weight average (M_w) but higher than the number average molecular weight (M_n). In particular the first of these two equations (1) gives the so-called viscosity average molecular weight M_v. The exact relationship between M_w and M_v can be established without

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difficulty, however for some reason it is generally considered that M_v is "almost equal" to M_w and this non-existent "equality" is often applied uncritically.

Meanwhile a number of authors [1, 3, 4] have been occupied by the problem of the kind of molecular weight given by different methods of measurement. It is evident however that the interconnexion between these molecular weight methods has not been made sufficiently clear, as a result of which in the literature of polymer science there are widespread errors concerning the values of the various average molecular weights and also "general equations" of the type

$$[\eta] = K_n M_n^a \text{ and } [\eta] = K_w M_w^a \tag{1a}$$

by means of which not only M_n and M_w are calculated but also polydispersity. In fact equations of this type do not hold because they cannot contain a pre-exponential constant.

The purpose of the present communication is twofold: first to prevent the arbitrary use of equations of the type of (1a) and to do away with the confusion between M_w, M_v and certain other average molecular weights and secondly to put forward, on the basis of an analysis of the M–K–H equations, a number of absolutely rigid criteria of polydispersity, which are a generalization of some particular variants [5, 6].

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THE PHYSICAL MEANING OF THE M-K-H EQUATIONS

The M–K–H equations describe different types of hydrodynamic homologies. The latter embraces chemical homology and in the most general sense can define as monotonic the change in hydrodynamic properties of macromolecules with increase in molecular weight. These properties are obviously connected with dimensions and/or shape. As an illustration of this very general, though unfortunately sometimes badly understood position we shall analyse the M—K–H equations starting from the fundamental equations of Einstein and Stokes for suspensions of rigid particles (for the strict theory see references (1, 2, 7, 8)). Einstein's equation can be reduced to the form

$$[\eta] = \nu V \tag{4}$$

where V is the specific volume of the disperse phase and ν is the viscosity increment, a dimensionless quantity which is characteristic only of the shape of the molecule. In particular, for spherical particles $\nu = 2{\cdot}5$. (It should be noted that in the c.g.s. system the dimensions of $[\eta]$ are cm^3/g whereas in practice the units of $[\eta]$ are $dl/g = 100 cm^3/g$. It is always necessary to remember to calculate ν in accordance with the experimental values of $[\eta]$.) It is immediately evident from equation (4) that a hydrodynamic homology can be defined by the dependence of ν or V, or of both these quantities simultaneously, on M. For rigid (solid) particles of identical composition obviously $V = \text{const}$. If the homology is such that the particles grow with increase in M, remaining identical with the another, $[\eta]$ will be independent of M if there are no asymmetric or very large particles. If the asymmetry i.e. ν, changes with M, then $[\eta]$ can either

increase or decrease with increase in M depending on whether the asymmetry increases or decreases with increase in M. A typical example of a decrease in ν with increasing M is the side by side aggregation of elongated rod-like particles. In this case it is possible in principle to obtain equations of the type $[\eta] \sim M^{-1}$ or even $[\eta] \sim M^{-2}$.

Values of ν have been calculated by Simha [9] and tabulated [10] for elongated and flattened ellipsoids of revolution as a function of the axis ratio p. Table 1 shows only the extreme values of the exponent a for "degenerated" ellipsoids, i.e. elongated (rod-like) and flattened (disk-shaped) cylindrical particles. We do not cite the calculations that can easily be made by substitution of the real particle by the effective hydrodynamic sphere described by the given particle around its centre of gravity as a result of rotational Brownian movement. (This automatically assumes that the gradient dependence of [η] is excluded.)

For ellipsoids the exact equations of Simha for ν can be approximated to by exponential equations of the M–K–H type with intermediate values of a.

TABLE 1. VALUES OF a IN THE M–K–H EQUATIONS FOR SOLID, RIGID PARTICLES FOR DIFFERENT TYPES OF HOMOLOGY

Shape of particles	Type of homology	a
Elongated cylinders	Height h=const; diameter D is proportional to M	−2
	h =const; $D \sim M$	−1
	D=const; $h \sim M$	+2*
Disks	h =const; $D \sim M$	$+\frac{1}{2}$
	D=const; $h \sim M$	−1
Any shape	Particles grow without change in shape	0

* More accurate calculation shows that here $[\eta] \to KM^2/\ln M$ and $a \to 1{\cdot}7$ [9].

However a will always be >0 if the assymmetry increase with increasing M and <0 if it decreases with increasing M.

We do not present Table 1 as any form of paradox. In recent years more and more importance is attached to investigations of biological polymers and their synthetic models (polypeptides and polyribonucleotides) for which some types of homology for rod-like particles are satisfied in an almost pure form. And it is in these very cases that careless application of the "general equations" mentioned in the introduction, can lead to gross errors.

For linear polymers, strictly speaking, V should be substituted by the effective specific volume, which is obviously equal to

$$V_{\text{eff}} = \frac{4/3\pi R^3 N}{M} \tag{5}$$

where N is the Avogadro number and R is the radius of inertia. Often the calculation of ν used in practice for linear polymers, it stands to reason, is devoid of meaning because the specific volume used in equation (4) has nothing in common with V_{eff} and ν already does not characterize the shape of a particle which however changes to some extent with M. The asymmetry of statistical coils having the shape of a triaxial ellipsoid, slowly increases. In the contemporary hydrodynamic theories it is considered however that ν=const. and all changes in $[\eta]$ and f are related to V_{eff}. Hence here the homology is due to increase in the effective volume. In so far as $R^2 \sim M\alpha^2$, where α is Flory's swelling parameter [1], which in turn is approximately proportional to M^{ε} with $0 \leqslant \varepsilon \leqslant 0{\cdot}13$, then $V_{eff} \sim M^a$ and $[\eta] \sim M^a$ with $a = \frac{1}{2} + 3\varepsilon$.

Therefore for linear polymers a should not exceed 0·9 (normally it does not exceed 0·8) and it can reach unity only for swollen coils [2]. The occurence of $a > 1$ indicates that there is structural rigidity. The exponent a, in spite of widespread misconception, bears not the slightest relationship to internal rigidity, i.e. to the potential barrier hindering rotation of the monomer units about the bonds of the backbone.

By analogy with (4) Stoke's law, which for spherical particles takes the form $f_0 = 6\pi\eta_0 r = 6\pi\eta_0 (\frac{3}{4} VM/\pi N)^{\frac{1}{2}}$, where η_0 is the viscosity of the solvent, can be written in the general form

$$f/\eta_0 = \Phi(p)\,(VM)^{\frac{1}{2}} \tag{6}$$

where the axis ratio function $\Phi(p)$ has the same meaning as ν. Usually in place of $\Phi(p)$ Svedberg's so-called asymmetry coefficient is written, denoted by f/f_0, the ratio of f for the real particle to $f\,(=f_0)$ for a spherical particle of the same density. $\Phi(p) \equiv 6\pi (f/f_0)\,(\frac{3}{4}\pi N)^{\frac{1}{2}}$. Values of f/f_0 have also been tabulated [10]. Hence the dependence of f on M can also be subdivided into the dependence of shape $[\Phi(p)]$ or specific volume V on M.

It is easy to show that $\Phi(p) = \text{const.}\, \nu^{\frac{1}{3}}$, from which values of b can be found for all the types of homology shown in Table 1. The connection between b and a is given by the equation.

$$b = \frac{1}{3}(a+1) \tag{7}$$

For flexible, linear macromolecule it is again necessary to substitute V in (6) by V_{eff}. Here $\Phi(p)$, like ν, has little meaning and is applied as a constant This brings us back to the form of Stoke's law

$$f/\eta_0 = PR \tag{8}$$

where P, calculated on the basis of strict theory, is a coefficient which for the "average" polymer is equal to 5·13 and varies little with the detailed structure of the coil, and $R \sim M^{\frac{1}{2}}\alpha$.

Consequently for coils

$$b=\frac{1}{2}+\varepsilon \text{ and } a-b=2\varepsilon \tag{9}$$

or, as before, $b=\frac{1}{2}(a+1)$. We shall not here touch upon possible complications connected with the permeability of the coils, where deviation from the simple rule (9) is possible [2, 11]. We shall mention only that at low values of M, when the molecules have not yet attained a "stable" coil configuration, the graphs of $\log[\eta]$–$\log M$ are curved characteristically because here both ν and V_{eff} vary simultaneously and markedly with M.

THE DISTRIBUTION FUNCTION AND AVERAGE MOLECULAR WEIGHTS

We shall start from the normalized distribution functions, putting the number fraction, dn, of macromolecules within the interval $M-M+dM$ as

$$dn=q_n(M)\,dM \tag{10}$$

and the weight fraction, dw, of macromolecules in the same interval, as

$$dw=q_w(M)dM \tag{11}$$

$q_n(M)$ and $q_w(M)$ are the number and weight distribution functions. Since for both functions $\int_0^\infty q(M)dM=1$ (normalization condition)

$$q_w(M)=\frac{M}{M_n}q_n(M) \tag{12}$$

The values of $m_q=\int_0^\infty M^q q_n(M)dM$ are called the moments of the distribution and are mean values of M to the qth degree. In particular $M_n=m_1$, being the "simple" mean or the average molecular weight of the first order. In accordance with this there can be two types of average molecular weight.

(1) *The* q*-average molecular weight* M_q. These weights are essentially the ratios of consecutive moments

$$M_q=m_q/m_{q-1} \tag{13}$$

in particular $M_w\equiv M_2=m_2/m_1$, $M_z\equiv M_3=m_3/m_2$ etc. In other words the weight average molecular weight is the ratio of the mean square to the mean, the Z-average (M_z) is the ratio of the mean cube to the mean square etc. We shall not dwell on the generally known physical principles of deriving averages from which the terms "weight average" and "number average" are derived.

The index q can be negative, fractional or irrational. Measurements usually give q-average molecular weights corresponding to integral values of q, from the ratio of which the molecular weight distribution can be reproduced. Thus for example, in the simplest case of the Schultz exponential distribution

$$q_n(M)=\frac{a^{k+1}}{\Gamma(k+1)}M^k e^{-aM} \tag{14}$$

the distribution parameters α and k are easily found by comparison of two M_q's, $M_{q'}=(q+k)/\alpha$. For narrow fractions ($k \geqslant 4$) the difference between M_n and M_w is very small.

(2) *Hydrodynamic average molecular weights.* The other principle of averaging is a generalization of the method of mean square parameters. It is clear that the square root of the index q from m_q will also be an average molecular weight, however such molecular weights will bear different relationships to one another than is the case for q-average weights. Their general equation takes the form

$$M_p=\left[\int_0^\infty M^p q_w(M)\,dM\right]^{1/p} \tag{15a}$$

$$M_t=\left[\int_0^\infty M^t q_w(M)\,dM\right]^{1/t}. \tag{15b}$$

For reasons that will become clear from what follows the second of these weights can be called the "hydrodynamic average" molecular weight.

VISCOSITY AVERAGE MOLECULAR WEIGHT

The intrinsic viscosity is intrinsically a weight average characteristic, i.e.

$$[\eta]\equiv[\eta]_w=\int_0^1[\eta]\,dw=\int_0^\infty[\eta]\,q_w([\eta])\,d[\eta]=\int_0^\infty[\eta]\,q_w(M)\,dM\,. \tag{16}$$

since $q_w([\eta])d[\eta]=q_w(M)dM$.

If within the limits of a given homologous series the M–K–H relationship is satisfied then

$$[\eta]=K_\eta\int_0^\infty M^a q_w(M)\,dM \tag{17}$$

and the viscosity average molecular weight is given by

$$M_v=\left(\frac{[\eta]}{K_\eta}\right)^{1/a}=\left[\int_0^\infty M^a q_w(M)\,dM\right]^{1/a}=\left[\frac{1}{M_n}\int_0^\infty M^{a+1}q_n(M)\,dM\right]^{1/a} \tag{18}$$

Experimentally M_v is obtained by application of the first of equations (1), the parameters of which were obtained on narrow fractions (in this case, in fact, $M_w \approx M_v$), for determination of the molecular weight of polydisperse materials.

It is immediately evident from (18) that $M_w=M_v$ only when $a=1$. When $a<1$, $M_v<M_w$ but reaches M_n only when $a=-1$ (a case which, as we have seen, is quite possible) and when $a>1$, $M_v>M_w$. We have already stressed the increasing role of biopolymers and at the present time it is already possible to name some homologous series where the latter inequality should be satisfied. How far M_w differs from M_v, i.e. to what extent is it incorrect to substitute the one average by the other already needs to be solved in general terms. We shall derive a

suitable estimation, which is quite typical, for the Schultz distribution (14) which is convenient because its moments of any order are expressed elementarily in terms of gamma functions. In a similar way estimations can be made of other types of distribution also. The moment of order q of distribution (14)

$$m_q = \frac{\Gamma(q+k+1)}{\Gamma(k+1)} \cdot \frac{1}{a^q} \tag{19}$$

and correspondingly

$$M_v = [M_n^{-1} m_{a+1}]^{1/a} = \frac{1}{a}\left[\frac{\Gamma(a+k+2)}{\Gamma(k+2)}\right]^{1/a}. \tag{20}$$

Let us consider the relationships

$$M_w : M_v = (k+2) : \left[\frac{\Gamma(a+k+2)}{\Gamma(k+2)}\right]^{1/a} \equiv f_w \tag{21a}$$

$$\text{and } M_n : M_v = (k+1) : \left[\frac{\Gamma(a+k+2)}{\Gamma(k+2)}\right]^{1/a} \equiv f_n. \tag{21b}$$

These relationships have the following meaning. If we wish to pass from the indisputable equation

$$[\eta] = K\eta\ M_v^a \text{ to equation (1a)}, \quad [\eta] = K_n M_n^a \text{ or}$$

$$[\eta] = K\eta\ M_w^a \text{ with the same value of } a \text{ (cf. Introduction)},$$

then

$$f_w = K_w/K_h \text{ and } f_n = K_n/K_v \tag{22}$$

From which it is soon evident that equation (1a) is incorrect because f_w and f_n are essentially funtions of the distribution parameter k. In other words the application of equation (1a) is admissible only within the limits of monotypical (k = const.) distributions. Equations (21) can be simplified only when a is an integer. For illustration Table 2 shows values of f_n and f_w within the limits $-1{\cdot}7 \leqslant a \leqslant +1{\cdot}7$ for five Shultz distributions with different values of k, embracing all the types of polydispersity met with in experimental work.

We see that f_n is very strongly dependent on k and the formula $[\eta] = K_n M_n^a$ must not be used even for a series of related distributions such as $0 \leqslant k \leqslant 1$ (radical polymer with chain termination by both recombination and disproportionation). The position is a little better in the case of f_w but even here the formula $[\eta] = K_w M_w^a$ is admissible only within the limits $0{\cdot}7 \leqslant a \leqslant 1{\cdot}2$ and its thoughtless application can lead to false deviation in log–log plots of $[\eta]$ against M_w and to other errors. Figure 1 is a histogram for the estimation of M_w/M_v at various values of a and k. If M_w and M_n are known* it may be used for the

* In general, for the estimation of any of the three molecular weights in the series $M_n - M_v - M_w$ if the other two are known.

estimation of M_v. By extrapolation of the results of Table 2 and Fig. 1 to other distributions we can reach the general conclusion that the difference between M_v and M_w is greater the wider the distribution and the greater the absolute value of $(1-a)$. For analitycal purposes (determination of the size of the coils, the nature of the homology etc.) graphical presentation of the results by $\log[\eta] = F(\log M_w)$ is inadmissible in any circumstances.

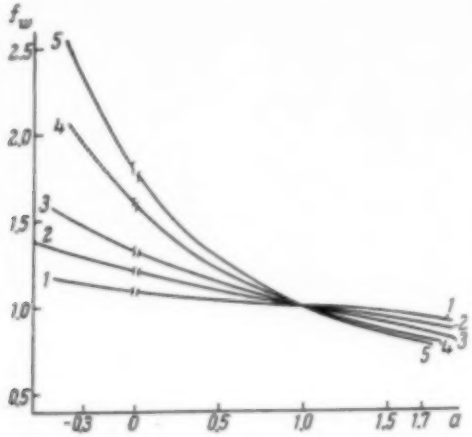

FIG. 1. Values of M_w/M_v as a function of a for different exponential distributions. The parameter k is a measure of polydispersity, $M_w:M_n = k+2/k+1$. (1) $k=4$; (2) $k=1$; (3) $k=0$; (4) $k=0{\cdot}75$; (5) $k=0{\cdot}95$.

In conclusion we shall consider the "disappearance" of M in the bottom left hand corner of Table 2. If we continue to express it in terms of gamma-functions we should obtain here $M_v<0$, which has no physical meaning. If we reject the idea of quasi-continuous distributions and replace the integration by summation we should obtain $M_v \to M_0$, the molecular weight of the monomer. The fact is that in a (model, we stress this) Schultz distribution when $k \to -1$, $M_n \to 0$. But because when $a < -1$, $M_v < M_n$, it is not surprising that M_v falls off with decreasing k more rapidly than M_n.

Additional complications arise with branched polymers if the degree of branching increases with M. In these circumstances the M—K—H relationships are no longer satisfied and M_v is related to M_w and M_n in a more complex manner. These problems, which were analysed in detail by Mussa [12] we have discussed elsewhere [13].

OTHER HYDRODYNAMIC AVERAGE MOLECULAR WEIGHTS AND THE CRITERIA OF POLYDISPERSITY RELATED TO THEM

We should obtain averages similar to the M_v type by using the M—K—H equations for the other weight average hydrodynamic parameters s and D. For this

TABLE 2. VALUES OF f_n AND f_w FOR DIFFERENT TYPES OF DISTRIBUTION HOMOLOGY

Type of distribution	a, and type of homology																	
	$-1{\cdot}7$ Rigid rods; diameter increases ~ M		$-1{\cdot}0$ Rigid rods; diameter ~ M		$-0{\cdot}333$ Rigid ellipsoids; asymmetry decreases with increasing M		$+0{\cdot}333$ Strongly branched or semi-rigid polymer		$0{\cdot}5$ Linear polymer at the θ-point		$0{\cdot}80$ Linear polymer in a good solvent		$1{\cdot}0$ Swollen coils; semi-rigid molecules of the cellulose type		$1{\cdot}333$ Semi-rigid polymer with macromolecules in the shape of a zigzag or elongated ellipsoids		$1{\cdot}7$ Rigid ellipsoids h ~ M	
	f_n	f_w	f_n	f_w	f_n	f_w	f_n	f_w	f	f_w	f_n	f_w	f_n	f_w	f_n	f_w	f_n	f_w
$k=4$ (Very narrow fraction)	1·08	1·3	1	$\frac{6}{5}$	0·95	1·14	0·89	1·07	0·863	1·036	0·85	1·02	$\frac{5}{6}$	1	0·812	0·976	0·78	0·94
$k=1$ (recombination distribution [13])	1·25	1·875	1	$\frac{3}{2}$	0·86	1·29	0·755	1·13	0·725	1·09	0·685	1·03	$\frac{2}{3}$	1	0·633	0·950	0·60	0·90
$k=0$ (Flory's equilibrium distribution [1])	1·91	3·82	1	2	0·735	1·47	0·595	1·19	0·568	1·14	0·525	1·07	$\frac{1}{2}$	1	0·465	0·93	0·43	0·86
$k=-0{\cdot}75$ (Tung's variant of distribution for polyethylenes[18])	M_v Not expressed as gamma-function(see explanation in text)		1	5	0·39	1·95	0·26	1·30	0·243	1·215	0·215	1·08	$\frac{1}{5}$	1	0·18	0·90	0·16	0·81
$k=0{\cdot}95$ (the same)	,,		1	21	0·11	2·34	0·066	1·38	0·063	1·29	0·052	1·10	$\frac{1}{21}$	1	0·042	0·88	0·037	0·785

* In this column $f_w = M_w/M_v$.

reason average molecular weights of the type of (15b) we have suggested should be called "hydrodynamic averages". Their special feature, in comparison with q-averages, lies in the fact that their order, i. e. the value of the exponent a (or b, or $(1-b)$, see below), is determined by the structure of the polymer and the nature of the solvent.

Let us consider the quantities (cf. (2) and (3))

$$M_D=(D/K_D)^{-1/b}=\left[\int_0^\infty M^{-b}q_w(M)\,dM\right]^{-1/b} \tag{23a}$$

and

$$M_s=(s/K_s)^{1/(1-b)}=\left[\int_0^\infty M^{1-b}q_w(M)\,dM\right]^{1/(1-b)} \tag{23b}$$

and call them the diffusion average and sedimentation average molecular weights respectively. It is evident that M_s has the same kind of properties as M_v on substituting a by $(1-b)$ and they can be found from Fig. 1 and Table 2. As regards M_D, at $b=1$ it coincides with M_n, and for its general analysis formula (23b) should be replaced by the identical

$$M_D=\left\{\frac{M_n}{\int_0^\infty M^{1-b}q_n(M)\,dM}\right\}^{1/b}. \tag{24}$$

Since the moment in the denominator of this expression at $b>0$ is less than M_n, usually $M_D<M_n$. Taking again the Schultz distribution we obtain

$$M_D=\frac{1}{\alpha}\left\{\frac{\Gamma(k+2)}{\Gamma(k+2-b)}\right\}^{1/b}. \tag{25}$$

By substituting a series of values in the range $-0{\cdot}23\leqslant b\leqslant 0{\cdot}9$, corresponding to limits of a from $-1{\cdot}7$ to $+1{\cdot}7$ (equation (7)) it can be seen that $M_D<M_w$ (and could be equal to M_w only at $b=-1$, which is impossible), and in general is greater than M_n. Only for swollen coils, when $b=1$ can $M_D=M_n$.

It should be emphasized that the hydrodynamic average molecular weights that we have introduced correspond to weight average values of s and D. In principle there are methods of calculation of other average values of these parameters (see in this connexion [3, 4, 14]) and there will be hydrodynamic average molecular weights of other orders corresponding to these. These other weights are, however, much less convenient than those under discussion.

By substituting D_w and s_w in the Svedberg equation

$$M=\frac{s}{D}\,\frac{RT}{1-V\rho} \tag{26}$$

the so-called "double weight average" molecular weight M_{ww} is obtained, which is often stated to be "almost equal to the weight average", with absolutely no

foundation. This is an even greater fallacy than the affirmation that $M_w \approx M_v$ (Meyerhoff [15] first pointed this out). Simple substitution

$$M_{ww} = \frac{\int_0^\infty M^{2-b} q_n(M)\, dM}{\int_0^\infty M^{1-b} q_n(M)\, dM} \tag{27}$$

shows that M_{ww} is a q-average weight of order 2-b. At $b = 0{\cdot}5$ $M_{ww} = {}^1/_2 (M_w + M_n)$ and at $b > 0{\cdot}5$ it is closer to M_n than to M_w, becoming equal to M_n for swollen coils ($b = 1$). For strongly branched and rigid globular molecules M_{ww} is greater but it is almost never as large as M_w. (This should occur when $b = 0$, i.e. $a = -1$). Being a q-average, M_{ww} in the Schultz distribution gives the expression

$$M_{ww} = \frac{k+2-b}{\alpha} \tag{28}$$

and is easily expressed in analytical form for any other (analytical) distribution.

We can now pass on to a consideration of the criteria of polydispersity.

CRITERIA BASED ON SOLVENT VARIATIONS

The dependence of the hydrodynamic averages and M_{ww} on the shape of the molecules and the nature of their interaction with the solvent opens up a completely new possibility of estimating polydispersity by the method of solvent variation. Since in this way the exponents a or b are altered we obtain a selection of average weights, or moments, of different orders, and from the relationships between these the molecular weight distribution can be plotted. It is obviously desirable to try to obtain the largest possible variation of the exponents, i.e. to carry out measurements both in very poor (close to Θ) solvents and in thermodynamically good solvents. This method is particularly convenient when it is possible to select solvents in which the structural rigidity of macromolecules, possessing secondary and tertiary structure, is destroyed. A typical example is the "denaturing" of synthetic α-polypeptides [16] which occurs in the solvent-induced transformation of the α-spiral (rigid rod, $a = 1{\cdot}7$, $b = 0{\cdot}9$) to the statistical coil ($a \approx 0{\cdot}89$, $b = 0{\cdot}63$). Similar transformations are also possible for some synthetic vinyl polymers [17].

In itself the method of calculation is not more difficult than the determination of polydispersity by the q-average but it should be remembered that whereas the experimental range of q-average molecular weights for a given polymer is limited (even with equilibrium ultracentrifugation [2]), here we can, in principle, use any number of solvents with different values of a and b. As was pointed out by Lundberg and Frisch [5], who first suggested the application of this method to M_v, the existence of such a wide selection enables an objective choice to be made for a given polymer of the analytical distribution function or plotting the distribution from the moments by the method of generating functions.

For these calculations either the hydrodynamic average molecular weights themselves can be used or the corresponding moments, found directly by experiment:

$$m_\eta = [\eta]/K_\eta = \int_0^\infty \mathrm{M}^a q_w(\mathrm{M})\, d\mathrm{M}\,, \tag{29}$$

$$m_D = D_w/K_D = \int_0^\infty \mathrm{M}^{-b} q_w(\mathrm{M})\, d\mathrm{M} \tag{30}$$

$$m_s = s_w/K_s = \int_0^\infty \mathrm{M}^{1-b} q_w(\mathrm{M})\, d\mathrm{M}\,. \tag{31}$$

By measuring any of these moments or M_{ww} at different values of a or b, q_w (M) or q_n (M) can be "deciphered". In the case of the Schultz distribution the decipherment will involve the calculation of k and α.

The ratio of an arbitrary pair of values of M_{ww} or of moments is a rapid, quantitative criterion. The connexion between these ratios and the inhomogeneity parameter of Schultz, $U = (\mathrm{M}_w/\mathrm{M}_n) - 1$ can readily be found for any analytical distribution. Here, for the purpose of illustration, we shall limit ourselves to the Schultz distribution. According to (28) the ratio of two values of M_{ww} is equal to $(k+2-b_1)/(k+2-b_2)$ $(b_2 > b_1)$ and a new homogeneity parameter can be introduced.

$$U_{ww} = \frac{\mathrm{M}_{ww}^{(2)}}{\mathrm{M}_{ww}^{(1)}} - 1 = \frac{b_2 - b_1}{k+2-b_2}\,. \tag{32}$$

Always for $k > 0$

$$U = \frac{1}{k+1} > U_{ww}$$

because $b_2 - b_1 < 1$ and $2 - b_2 \geq 1$.

Similary for different values of a $(a_2 > a_1)$ an inhomogeneity parameter can be introduced.

$$U_v = \frac{\mathrm{M}_v(a_1)}{\mathrm{M}_v(a_2)} - 1 = \frac{a_1 - a_2}{2}\, U\,[^8]. \tag{33}$$

The inhomogeneity parameters U_D and U_s will have similar meanings and formulae of this type can be derived to express their relationship to U.

CRITERIA BASED ON "CROSSED" COMBINATIONS OF MOMENTS

A disadvantage of these relationships is their lower sensitivity in comparison with the ratios of q-average molecular weights (where q is an integer) of different orders ($U_{ww} < U$, $U_v < U$ etc). Greater accuracy can be attained from combinations of the moments m_D, m_s and m_η, measured in the same or different solvents. For linear polymers it is most convenient to use values obtained in good solvents

where the differences in order of the moments being compared become maximal. For example, at $a=0{\cdot}8$ and $b=0{\cdot}6$ for the Schultz distribution

$$\frac{m_\eta}{m_D}=\frac{m_{1,8}}{m_{0,4}}=\frac{\Gamma(k+2{,}8)}{\Gamma(k+1{,}4)}\alpha^{-1\cdot4}, \tag{34}$$

and α can be eliminated by making three measurements. If however k is known equation (34) gives the distribution parameter a directly.

It should be noted that any combination of m_D, m_s and m_η enables new types of hydrodynamic averages to be determined. For example the average molecular weight

$$\mathbf{M}_{\eta/D}=(m_\eta/m_D)^{1/(a+b)}$$

corresponds to the combination given in equation [34].

The molecular weights calculated by the formulae of the Flory-Mandelberg theory [1], reduced to the form

$$A=D^3[\eta]\,\mathrm{M} \text{ and } B=s^{3/2}[\eta]^{\frac{1}{2}}\mathrm{M} \tag{35}$$

where A and B are constants for a given polymer-solvent system, are also more complex types of hydrodynamic averages and can (in principle) be used for analyses of polydispersity.

OTHER POSSIBILITIES

Recently Schumaker [6] on three specific examples discussed the possibility of direct determination of the distribution function q_w (M) by a combination of high-speed ultracentrifugation, giving the distribution according to the sedimentation coefficient $q_w(s)=q_w(\mathrm{M})/(ds/d\mathrm{M})$ [2] with measurements of [η]. For new polymers for which the parameters of the M—K—H equations are unkown this calculation of $q_w(s)$ in terms of q_w (M) can be achieved by finding the correlation between s and [η] (which is equivalent to calculating M by the second of equations (35) or by calculating the moments of the molecular weight distribution be means of adequate combinations of [η] (or D) with the moments of the distribution $q_w(s)$. Schumaker's method can be made quite general if ordinary fractionation (with measurement of [η] of the fractions) is combined with determination of $q_w(s)$. The transition from the integral curve of w([η]) and $q_w(s)$ to q_w (M) is brought about in the elementary way by means of the second of equations (35) (the parameter B depends only on the universal temperature constant, η_0 and $1-V_\varrho$ [1]).

With sufficiently accurate fractionation (let us say 10 fractions) to each seperate weight fraction $w([\eta])$ there is a corresponding weight fraction $w(s)=\int_0^\infty q_w(s)\,ds$, and the problem reduces to the calculation of M from [η] and s at the same values of w (Fig. 2). While not discussing in detail this possibility, which we propose to make use of elsewhere, we shall state its chief merits.

(1) Since the curve of $w(s)$ is in general with the curve of $w([\eta])$ the stepwise, integral fractionation curve can be smoothed out by correction according to

the first curve. In particular if the distribution is multimodal (having several maxima) it is easy to distinguish between the true and the false points of inflexion of the $w([\eta])$ curve.

(2) Separate measurements of molecular weight are not required and the method gives the distribution function q_w (M) as well as the parameters a and b.

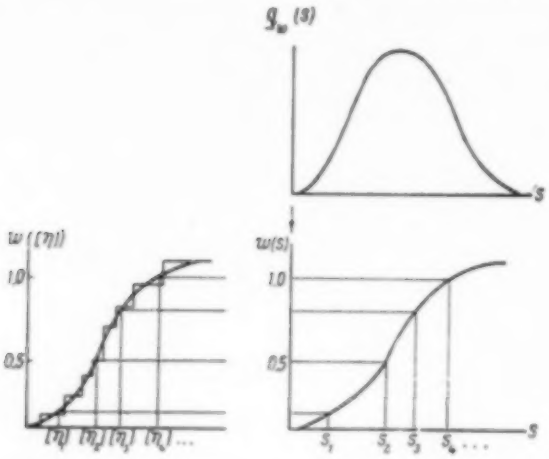

FIG. 2. A combination of "graphical" and ordinary fractionation for determination of the distribution functions q_w (M) according to $[\eta]$, and $q_w(s)$.

(3) The method does not require the function q_w (M) to be represented by a model.

Another possibility consists in a combination of $[\eta]$ with the coefficient of rotational diffusion.

$$\Theta = \frac{kT}{f_r} = K_\theta M^{-(1+a)}. \tag{36}$$

CONCLUDING REMARKS

We have shown that there is an almost infinite number of criteria of polydispersity based on the adequate use of average (preferably weight average) hydrodynamic characteristics. The main experimental problem here consists in the correct "preparation" of the method for determination of the parameters a and b and in the correct calculation of s_w in methods involving sedementation. The latter—in spite of Meyerhof's pessimistic statement [4]—with modern ultracentrifuges, fitted with phase-contrast plates as in the Lam or Philpot-Svenson systems, can be carried out rapidly and without difficulty. As regards the determination of a and b it is best to carry out measurements on narrow fractions when M_w practically coincides with M_v and M_n with M_{ww}. Another method is possible, in which s, D and $[\eta]$ are determined as functions of M_w for polymers with monotypical distributions and then, knowing the distribution function the average molecular weight corresponding to the given parameter is calculated.

CONCLUSIONS

The Mark–Kuhn–Houwink equation correlating the intrinsic viscosity and the translational friction coefficient with the molecular weight has been extended to any type of hydrodynamic homology including macromolecular coils of linear polymers with flexible chains, and rigid particles. The physical sense of the resulting exponents in the equation for $[\eta]$ has been analysed and a corresponding generalization has been made of the concept of the viscosity—average molecular weight. In order to correct widespread misconceptions an analysis has been made of the dependence of M_w upon the exponent a and upon the width of the molecular weight distribution, and the limiting cases have been indicated when M_v becomes greater than M_w or less than M_n. For the Schulz exponential distribution a histogram has been presented of the values of M_w/M_v for various M_w/M_n ratios. The histogram may be used to estimate the deviations of M_v from M_w also for other distributions. An analysis has been made of the relation between the so-called double weight average molecular weight and M_w and a new general concept of mean hydrodynamic molecular weights has been introduced. A detailed discussion has been made of the relation between the two mean hydrodynamic weights M_η and M_D and M_w and M_n. Three quantitative criteria have been suggested for polydispersity, based on comparison of various hydrodynamic mean values. Of these, one, called the method of solvent variation, generalizes the Frisch and Lundberg viscometric polydispersity criteria, the second is an analogue of the method of the q-mean weights and the third is based on a combination of fractionation and $[\eta]$ measurement with analysis of the non-fractionated polymer in the ultracentrifuge and does not require separate molecular weight determinations.

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THE FORMATION OF ISOTACTIC POLYMETHYLMETHACRYLATE DURING PHOTOPOLYMERIZATION IN THE SYSTEM METHYL METHACRYLATE—ZINC CHLORIDE*

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IN a recent paper by Fox *et al.* [1] it was shown that stereoregular polymers can be obtained by low-temperature, homogeneous, radical polymerization of certain acrylic and methacrylic esters. This is made possible by differences in the free energy of activation of the addition of the next monomer molecule to the growing polymeric radical, to give *d,d*—(*l,l*—) or *d,l*— sequence of the asymmetric carbon atoms. These differences in free energy result in a very strict selection being made of the energetically most favourable sequence of configurations of the asymmetric atoms. Fordham, McCain and Alexander [2, 3] reached a similar conclusion from a study of the radical polymerization of a number of halogenated vinyl ethers. We have shown [4] that a stereoregular polymer can be obtained by polymerization of methyl methacrylate in the solid state. It was also found that whereas at low temperatures syndiotactic chains (*d,l*— sequence of asymmetric carbon atoms) are formed in the liquidphase polymerization of methyl methacrylate, in the solid state the formation of isotactic chains (*d,d*— or *l,l*— sequence) becomes more favourable. For an explanation of the results obtained a suggestion was put forward concerning the effect of previous ordering of the molecules in the solid monomer on the thermodynamic parameters of the propagation reaction that determine the relative probabilities of *d,d*—(*l,l*—) and *d,l*—additions.

As a development of this work it was of interest to examine the effect on the molecular structure of the polymer chain of the presence of inorganic salts dissolved in the monomer, capable of altering and fixing the consecutive order in the polymeric system. With this objective we have photopolymerized methyl methacrylate previously saturated with zinc chloride.

The experiments were carried out in the following manner. Carefully purified and dried methyl methacrylate and calcium metal turnings (drying agent) were placed in ampoule 1 (Fig. 1), anhydrous zinc chloride in ampoule 2 and a weighed quantity of photosensitizer, benzoyl peroxide (0·3% on weight of

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monomer), in the quartz vessel 3. Then with tap 4 shut the apparatus was pumped out to high vacuum and by cautiously heating ampoule 2 to 200° the $ZnCl_2$ was completely dehydrated. Then the methyl methacrylate was degassed by repeated freezing *in vacuo*, after which the monomer was distilled from ampoule

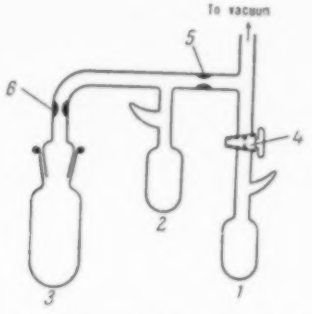

FIG. 1. Polymerization apparatus.

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1 on to the anhydrous zinc chloride in ampoule 2. The apparatus was then sealed off from the vacuum system at the constriction 5 while under vacuum. In order to obtain a saturated solution the contents of ampoule 2 were shaken for 1 hr at 20°C. After settling, the clear solution of zinc chloride in monomer was poured into the quartz vessel 3 (the excess salt being left behind in ampoule 2) and the benzoyl peroxide was dissolved in it. Finally vessel 3, containing the complete reaction mixture, was sealed off at the constriction 6.

Photopolymerization was achieved by ultraviolet irradiation by a PRK-2 mercury lamp in a quartz thermostat filled with water. During polymerization the polymer formed separated in the form of a much swollen, clear gel. Complete solution of the polymer in excess monomer was probably prevented by the formation of complexes between the ester side groups and molecules of zinc chloride, which increase the rigidity of the macromolecules. The degree of conversion in separate experiments usually reached 20–30 per cent. The polymer was dissolved in acetone and then, in order to remove zinc chloride completely, it was reprecipitated from acetone by methanol several times.

When photopolymerization was carried out in the presence of excess zinc chloride, occurring as a solid phase, the nature of the process was not essentially altered. However, under conditions the formation of clear, polymer gel began directly on the boundary between the solution and the solid phase where the rate of polymerization appeared to be greatest. With increase in the degree of conversion polymerization proceeded mainly within the already-formed, clear polymer layer, the thickness of which continued to increase up to the disappearance of the odour of monomer.

The introduction of a small quantity of hydroquinone into the reaction mixture inhibits polymerization, as indicated by an increase in the induction period. This indicates that polymerization takes place by a radical mechanism.

Investigation of the properties of the polymethylmethacrylate obtained by photopolymerization of the monomer saturated with zinc chloride showed that in the main the macromolecules have the isotactic molecular structure. For example, the density of the polymer, measured by the gradient-tube method, was 1·22g/cm². The glass temperature measured by means of a dynamometric balance was ~65°. The corresponding properties of syndiotactic polymethylmethacrylate are quite different (density 1·18–1·19g/cm², glass temperature 115–135° [5, 6]). After precipitation by *n*-heptane from toluene solution and swelling in heptanone-2, our polymer crystallizes. The X-ray diffraction pattern of the crystallized sample coincides with that shown in reference [4].

Thus by radical polymerization of methyl methacrylate saturated with zinc chloride, at room temperature, sufficiently strict stereoregulation is provided to lead to the formation of crystallizable, isotactic polymer.

For an explanation of these results let us examine the mechanism of selection of the spatial configuration of the asymmetric atoms that are realized in each separate propagation step in the polymerization of an unsymmetrical vinyl monomer. It is known that the last, reactive unit in a polymeric radical is either planar in shape or has the shape of a very flattened pyramid with the carbon C_1 (Fig. 2) at the apex [7]. As a result of thermal vibration atom C_1 passes through the plane of the base of the pyramid, appearing now below and now above this plane. The configuration at the penultimate atom C_2 and all the preceding

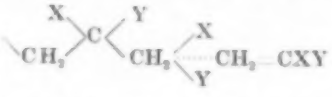

FIG. 2. Scheme of addition of the next monomer molecule to a polymer radical.

atoms is already fixed, each of them forms the centre of a corresponding tetrahedron. Fixation of the configuration of atom C_1 takes place at the moment of addition of the next monomer unit to the polymeric radical and the probability of the *d,l* or *d,d* configuration, due to the non-valence interaction of the substituents X and Y on atoms C_1 and C_2, can depend on the already settled configuration of the asymmetric atom C_2. If, for example, substituent X is a bulky or strongly polar group the mutual repulsion of these groups causes them to tend to take up positions as far from one another as possible during the process of addition of the next monomer unit. Then at each propagation step the chain should be set in that successive configuration of the asymmetric atoms C_1 and C_2 that, with the given conformation of the transition complex, corresponds to the maximal distance between the substituents X. Syndiotactic chains are formed in homogeneous low-temperature polymerization [3]. This means that in the case of free growth of the polymeric radical the *d,l*-sequence gives conditions of greatest separation of identical, repelling substituents.

At the same time it is easy to see from the above considerations that a change in conformation of the transition complex formed between the end of the polymeric radical and the next monomer molecule can, in principle, bring about a change

in the probability of *d,l*— and *d,d*—(*l,l*—) fixation. This can be seen from the diagram (Fig. 3) where two different conformations of the end of a polymeric radical are depicted. The carbon-atom chain lies in the plane of the diagram. The thick lines represent bonds directed upwards from this plane and the thin lines lie below the plane of the diagram. The dotted line denotes the bond being formed at the moment of addition of a new monomer unit, which is omitted from the diagram. Figure 3*a* shows the chain in the form of an extended planar zigzag. Let us assume that the groups interact and repel one another strongly.

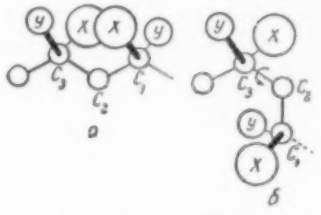

FIG. 3. Conventional illustration of two different end-group conformations of a polymeric radical. (The hydrogen atoms are not shown on the diagram.)

Then in case of the conformation shown in Fig. 3*a* the maximal distance between the substituents X will correspond to the structure in which one group X lies above the plane of the diagram and the other below this plane. On addition of the next monomer unit fixation of the configuration of atom C_1 must be such that the maximal distance between the substituents X is realized. Obviously in the situation depicted in Fig 3*a* the asymmetric atom C_1 becomes set in the configuration opposite to that of C_2, i.e. *d,l*-addition will occur. Let us now assume that in the intermediate state the end of the polymeric radical has the conformation depicted in Fig. 3*b*, which is obtained from conformation *a* by rotation of the group C_2C_1XY through 180° about the C_3—C_2 bond. In this case also the distance between the substituents X will be greatest if one is above and the other below the plane of the diagram (as is shown in the diagram). However this configuration of the asymmetric atom C means that the addition at C_1 will be of the same spatial configuration as at C_3, i.e. *d,d*— or (*l,l*—) addition will occur. In fact, if one imagines the group C_1C_2XY turned through 180° around the C_3—C_2 bond and conformation *b* extended to a planar zigzag it can be seen that the substituents X on atoms C_3 and C_1 occupy positions on the same side of the plane of the main chain.

This means that all the factors that affect the conformation of the transition complex can also affect the molecular structure of the polymer chain being formed. One of such factors is the effect of the crystalline field in the low temperature polymerization of a solid monomer [4].

The stereoregulation in the polymerization of methyl methacrylate in the presence of zinc chloride, described in this communication, is also probably

connected with a change in conformation of the transition complex as a result of complex formation between zinc chloride molecules and the side-chain ester groups of the radical and monomer, i.e. with a change in the spatial order around the active centre. It should be pointed out that of the number of geometric arrangements for methyl methacrylate it is quite impossible to consider isotactic addition with the formation of an extended planar zigzak of carbon atoms in the main chain because the bulky ester side groups cannot be accommodated on the same side of a planar zigzak. Isotactic addition can take place only if each monomer molecule in turn enters into the composition of the chain in such a way that after the addition of the $COOCH_3$ group rotation through a certain angle occurs. This corresponds to the growth of a chain in the form of a spiral. It is very probable that on polymerization in the presence of zinc chloride the necessary helical conformation is stabilized by the $ZnCl_2$ molecules, each of

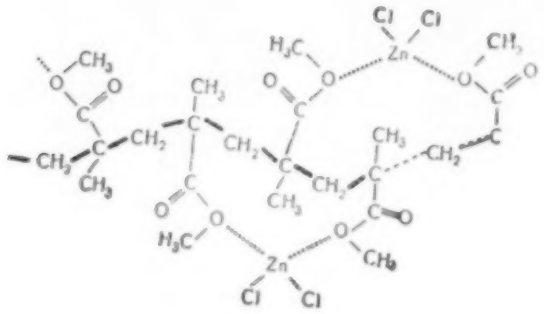

FIG. 4. Scheme in which zinc chloride molecules are included in the transition complex in the helical growth of a polymer chain.

which forms a coordination bond with two ester side groups. (Complexes of metal halides, capable of co-ordination, with the ester groups of polymethylmethacrylate are described in the literature [8]). In these circumstances, at the moment of addition of the next monomer molecule in the transition state, the necessary orientation of this molecule relative to the polymeric radical is fixed as a result of the complex-formation. The scheme shown in Fig. 4 represents the growth of a polymethylmethacrylate macromolecule in helical form. The zinc chloride molecule takes part in the formation of the transition complex.

When the polymerization is examined from the thermodynamic point of view it is evident that complex formation leading to fixation of the conformation of the transition complex in a manner suitable for isotactic addition must alter considerably the difference in free energy of activation for iso- and syndioaddition, probably chiefly as a result of the change in the entropy of activation. This enables stereoregulation to be achieved under radical polymerization conditions even without the use of low temperatures.

CONCLUSIONS

(1) It is shown that isotactic polymer is formed in the radical polymerization of methyl methacrylate at room temperature in the presence of zinc chloride dissolved in the monomer.

(2) The effect of the conformation of the reacting molecules in the transition state on the formation of the polymer chains is examined.

(3) A mechanism of stereoregulation in this system is proposed, based on the formation of complexes between the zinc chloride molecules and the ester groups of the polymeric radicals and monomer molecules.

Translated by E. O. PHILLIPS

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CHEMICAL CHANGES IN POLYVINYLCHLORIDE UNDER THE INFLUENCE OF IONIZING RADIATION*

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IT is well known that the action of ionizing radiation on polyvinylchloride (PVC) causes substantial changes in its physicochemical properties indicating that profound structural changes take place on radiolysis [1–4]. On irradiation of PVC dehydrochlorination with formation of conjugated double bonds takes place mainly, and also crosslinking of the chains [1]. The dehydrochlorination process is the same as that observed in thermal and photochemical degradation of this polymer [3]. The irradiated polymer acquires a colour of varying intensity (brown, green, violet, black), depending on the conditions of irradiation and the method of preparation of the polymer. This coloration has been explained [1] by the presence of free radicals "trapped" in the irradiated polymer and by the formation of conjugated double bonds as a result of the removal of HCL from the polymer. Free radicals of the type of $\sim CHCl-\dot{C}H-CHCl\sim$ and $\sim CH_2-\dot{C}Cl-CH_2\sim$ were in fact detected in PVC irradiated at 77°K in a nuclear reactor, by the method of electron paramagnetic resonance (EPR) [5]. Changes in colour on irradiation of PVC were also observed by us and it was noted that the colour decreased with the passage of time after irradiation. Since one of the uses of PVC is its application for the purpose of dosimetry [6] it was of interest to investigate the process of colour change. In this connexion an attempt was made to study the time dependence of the colour changes of PVC irradiated under various conditions and the molecular-structural changes involved.

RESULTS AND DISCUSSION

Samples of PVC in the form of a powder and films of thickness 40, 180 and 200 μ were irradiated *in vacuo* at 293° and 77°K and stored *in vacuo* and in air. The films were prepared from a solution of purified polymer in dichloroethane. Traces of solvent were removed by drying in a vacuum oven at 50°. Irradiation

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was carried out *in vacuo* ($\sim 10^{-4}$mm) at room temperature and at 77°K with high speed electrons of energy 200keV. The current density was 0·6μV/cm² for the infrared spectra. The irradiation time was varied between 10min and 3hr. The electron source was an electron-accelerator tube with a concentrated beam.*

The infrared spectra of the PVC films were measured in the region from 4000 to 650cm^{-1} in a Hilger spectrometer (Model 209, single-beam type) with a rock-salt prism. The absorption spectra were measured in an SF-4 spectrometer. The electron paramagnetic resonance spectra were measured in a spectrophotometer with high-frequency magnetic modulation, of the type described in reference [7]. The signal was recorded in the form of its first derivative. The sensitivity of the spectrophotometer was 5×10^{12} paramagnetic particles in the sample in measurements with the stable free radical diphenylpyerylhydrazyl.

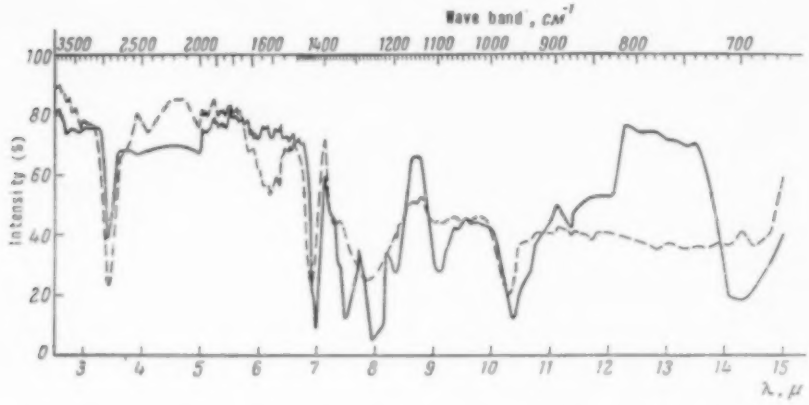


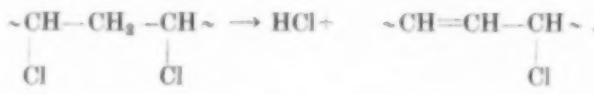
FIG. 1. Infrared spectra of polyvinylchloride (film thickness 40μ), unirradiated (continuous curve), and irradiated with high speed electrons *in vacuo* for 3 hr (dotted curve).

In the infrared spectrum of unirradiated PVC (Fig. 1) there is a strong band at 1256cm^{-1} which has no analogue in other vinyl polymers. This band is attributed to the chlorine atom, more correctly it is connected with the vibrations of the hydrogen atom in the —CHCl— group [8]. There is also a strong band at 1428cm^{-1} corresponding to the deformation vibration of the methylene group [9]. The absorption in the 1330cm^{-1} region relates to the vibration of the C—H group [9]. The band of average intensity at 1097cm^{-1} corresponds to the valency vibration of the C—C bonds of the carbon chain [9]. The band at 960cm^{-1} corresponds to the deformation vibration of the methylene group and to the valency vibration of the C—C bonds of the backbone [9]. The band at 698cm^{-1} is characteristic of the vibration of the C—Cl bond [9, 10].

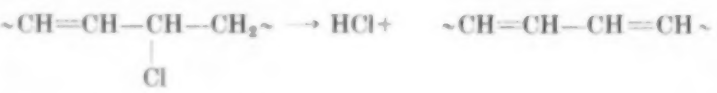
* We take this opportunity to express thanks to L. A. Vasilev, who carried out the irradiation of the samples in the electron tube.

In the spectra of PVC films (thickness 40μ) irradiated with high speed electrons *in vacuo* at room temperature for 3hr (current density 1·2μA/cm²) there are substantial changes in comparison with the spectrum of the unirradiated polymer (Fig. 1). The intensity of the bands at 1428, 1097, 960 and 698cm^{-1} is considerably lower and the bands at 1330 and 1256cm^{-1} are merged into a single, broad band at 1267cm^{-1} of much lower intensity. The decrease in intensity of the bands at 1256 and 698cm^{-1} indicate a decreased content of chlorine atoms in the PVC molecule, and of the bands at 1428 and 960cm^{-1}, a decrease in the content of methylene groups.

During irradiation in the absence of air, chemical changes take place, probably according to the following scheme [1].



The formation of one double bond increases the mobility of the chlorine atom in the α-position and this leads to further dehydrochlorination and the production of conjugated double bonds:



In the vibrational spectra of olefines containing conjugated diene and polyene groups there are bands in the region 1700–1500cm^{-1} [11] corresponding to the valency vibration of the double bonds. However it is not always possible to ascribe bands to the vibrations of individual double bonds because of the powerful interaction of the vibrations, occurring in conjugated systems. The presence of conjugated double bonds in irradiated PVC is confirmed by the appearance of a number of bands in the region 1720–1530 cm^{-1} (see Fig. 1). The coloration that appears in the films and powder and the shift of absorption in the ultraviolet spectrum toward the long wave region also indicate the formation of conjugated double bonds.

The absorption spectrum of PVC film of thickness 200μ (Fig. 2) plotted immediately after irradiation with high speed electrons *in vacuo* at room temperature for 10 minutes (current density 0·6μA/cm²) has three bands at 580, 650 and 700μ (green film). The absorption spectra of irradiated films change on storage, the the nature of the changes depending on the storage conditions (vacuum or air). In both cases the bands 580–700 cm^{-1} disappear (Fig. 2). The transmission in the region 550–1100mμ increases considerably on storage at room tempearature in air and after three weeks it approaches the transmission of the unirradiated polymer. On storing *in vacuo* there is an increase in transmission in the region ~650–850mμ, in comparison with freshly irradiated PVC, and starting at ~850mμ the transmission decreases. On storing *in vacuo* and in air the "optical density–wavenlength" curve shifts in the 250–450mμ region with little

change of shape and in the 550–750mμ region the height and shape of the curve alters. All this obviously indicates that there are changes not only in the concentration but also in the type of chromophoric groups present.

On prolonged storage of the irradiated PVC films a slow change in colour occurs up to the dark-red colour characteristic of thermally degraded PVC.

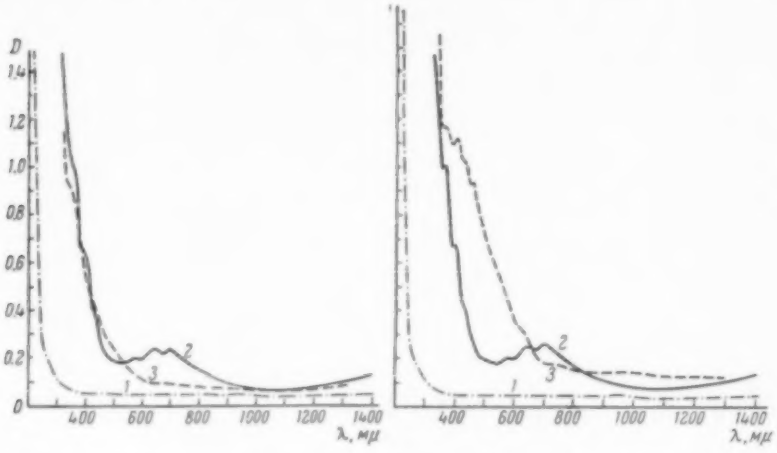


FIG. 2. Absorption spectra of polyvinylchloride films (thickness 200μ), irradiated *in vacuo*: (a) stored in air at room temperature; (b) stored *in vacuo* at room temperature: (1) unirradiated polyvinylchloride; (2) freshly irradiated polyvinylchloride; (3) irradiated polyvinylchloride after storing for three weeks. λ, wavelength; D, optical density.

The kinetics of the colour change of PVC films (thickness 180μ) irradiated with high speed electrons *in vacuo* at room temperature for 10 min. (current density 0·6μA/cm²) on storing at different temperatures (from −78 to 50°) in air, was studied by means of the absorption spectra.

At −78° the absorption curves remained practically unchanged for a long time. During the first 1–3 days storage at 0° a reduction in transmission in the 500–800mμ region occurs. On further storing (up to 1 month) a gradual increase in the transmission of the sample takes place.

In the first hour of storage at 20° (Fig. 3a) the transmission in the region 560–900mμ undergoes a small reduction then on further storage (up to 14 days) it increases considerably. In the first 30–40 min of storage of the PVC films at 30° there is a considerable decrease in transmission in the region ~600–1000mμ. On further storage (from 6 to 51 hr) the transmission in the region of ~600–760mμ increases and in the ~760–1000mμ region it decreases. The absorption curve shifts into the region of longer wavelengths and the intensity of absorption in the ~400–500mμ region increases. Heating an irradiated sample at 40° for only 30 min results in a considerable decrease in transmission in the ~640–1000mμ region (Fig. 3b). On further storage under these conditions the absorption curve shifts toward the longer wavelength side, the transmission in the ~640–820mμ

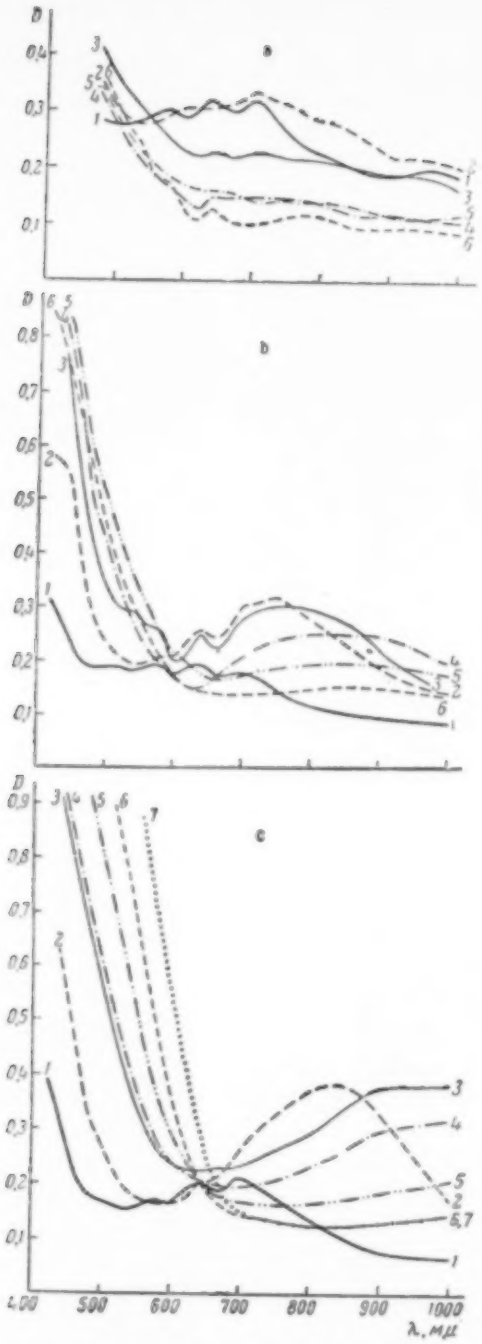


FIG. 3. Absorption spectra of irradiated polyvinylchloride films (thickness 180μ): stored (a) at 20°; (b) at 30°; (c) at 40°. (a) (1) freshly irradiated; (2) 4 hr; (3) 24 hr; (4) 48 hr; (5) 72 hr; (6) 14 days. (b) (1) freshly irradiated; (2) 30 min; (3) 1 hr; (4) 6 hr; (5) 19 hr; (6) 51 hr. (c) (1) freshly irradiated; (2) 25 min; (3) 1 hr; (4) 2 hr; (5) 6 hr; (6) 16 hr; (7) 33 hr.

region increases and in the 820–1000mμ region it decreases. The nature of the change in the curves on storage at 50° was the same as that at 40°.

The effect of the irradiation conditions on the nature of the transmission curves of the films was investigated. Figure 4 shows the absorption spectra of PVC films (film thickness 180μ) irradiated with high speed electrons at room

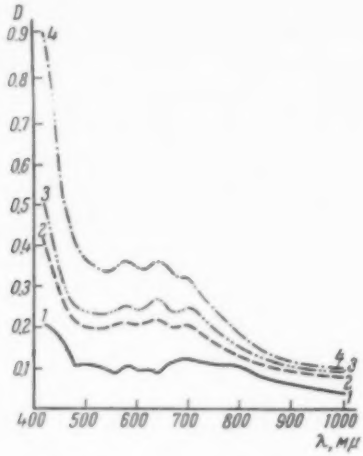


FIG. 4. Absorption spectra of polyvinylchloride films (thickness 180μ), irradiated *in vacuo* with high speed electrons for: (1) 5 min; (2) 15 min; (3) 20 min; (4) 40 min.

temperature (current density 0·6μA/cm²) for 5,12,20 and 40 min. An increase in irradiation time at the same current density leads to a fall in transmission of the films. In the spectrum of the irradiated samples there is strong absorption in the 420–460mμ region, the intensity of which increases with time of irradiation.

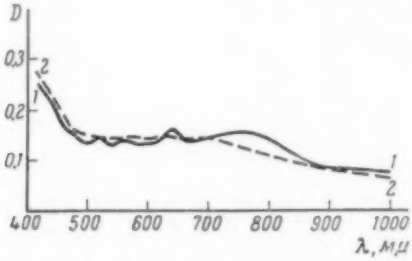


FIG. 5. Absorption spectra of polyvinylchloride films (thickness 180μ), irradiated *in vacuo* with high speed electrons (200 keV): (1) 10μA, 5 min; (2) 2μA, 25 min.

A similar increase in absorption with increasing time of irradiation also occurs at a current density of 0·11μA/cm². The transmission varies with the total dosage but is independent of the rate at which it is applied (within the limits of electron-beam intensity used, from 2 to 10μA, Fig. 4 and 5).

It is known that in the radiolysis of polymeric materials the first stage is that of ionization and exictation of the molecules, which lead to the rupture of chemical bonds with the formatioo of free radicals. In PVC such radicals could be [5]:

(1) radicals formed by the rupture of the C—H bond, $\sim CHCl\text{-}\dot{C}H\text{-}CHCl\sim$ and $\sim CH_2\text{-}\dot{C}Cl\text{-}CH_2\sim$;

(2) the radical formed by the rupture of the C—Cl bond, $\sim CH_2-\dot{C}H-CH_2\sim$. In structure this radical is close to that formed in polyethylene and should give an EPR signal with the corresponding superfine structure [5].

The presence in these materials of a significant quantity of radicals formed by the rupture of C-Cl bonds should have given a superimposed superfine structure on the lines of the other radicals which was not observed in our experiments, hence it may be considered that elimination of chlorine atoms must be accompanied by the elimination of an equivalent number of hydrogen atoms with the formation of double bonds or crosslinks between the molecules.

The EPR spectrum of PVC powder, irradiated *in vacuo* at 77°K with high speed electrons (at a current density of 0·6μA/cm²) for 10 min, obtained *in vacuo*

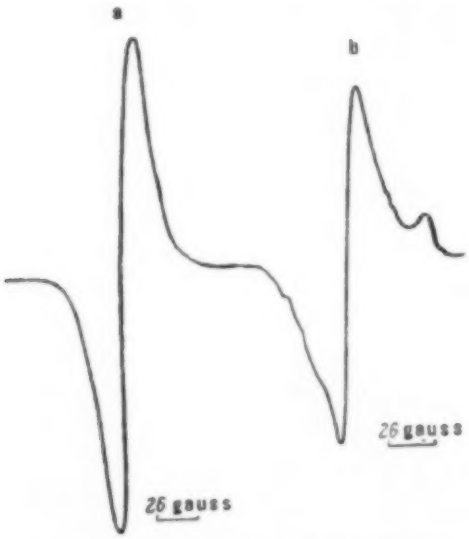


FIG. 6. EPR spectra of polyvinylchloride powder irradiated at 77°K: (a) *in vacuo*; (b) after keeping in air for 1 hr at room temperature.

without allowing the temperature to rise, shows a strong signal without superfine structure (Fig. 6a) and a band width of 26 gauss. The total concentration of radicals was $\sim 5 \times 10^{18}$ per gramme of PVC. On warming up the sample *in vacuo* to room temperature the strong signal was unchanged after one hour. Storing

the sample *in vacuo* at room temperature for a week resulted in an approximately sixfold reduction in the strength of the EPR signal. Evidently the number of radicals decreases gradually as a result of their recombination.

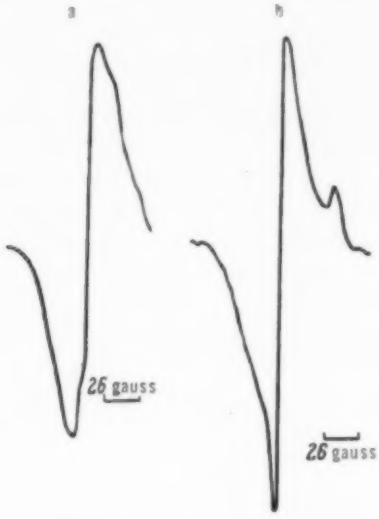


FIG. 7. EPR spectra of irradiated polyvinylchloride powder in air: (a) at room temperature; (b) at 77°K.

When the sample is allowed to come into contact with oxygen of the air at room temperature the strength of the signal decreases rapidly and it changes shape. A signal characteristic of peroxide radicals then appears (Fig. 6b). The rapidly diffusing oxygen evidently reacts with the free radicals and gives peroxide radicals of the type [1] $>\dot{C}H+O_2\rightarrow>CHO_2^{\cdot}$. With the passage of time the strength of the EPR signal of the primary and peroxide radicals decreases. Samples that have stood for a long time in air show only the peroxide-radical signal.

The EPR spectrum of PVC powder (irradiated under the same conditions but stored in air at 195°K), obtained at room temperature (Fig.7a) at first shows a fairly strong signal with marked resolution, the strength of which falls with time at a decreasing rate. After about 15 min the signal strength approaches a constant value. At 77°K in air a fairly strong signal is again observed (Fig.7b) and this has a fine structure. Evidently this is a signal characteristic of peroxide radicals, with better resolution. On repeated warming and freezing the sample shows the same characteristic EPR spectrum but with a lower intensity.

When irradiated samples of PVC are heated at 30° and 40° for an hour all the phenomena observed at room temperature are considerably accelerated. Successive heating of the sample for 1 hr at 50°, 15 min at 60° and 15 min at 70° did not result in any change in the signal. Further heating at 80° for 15 min

lead to a reduction in signal strength by a factor of 1·5. On heating subsequently at 90° (15 min) the signal falls to ~20 per cent of the original value and after heating at 100° (15 min), to ~5 per cent, without change in shape of the signal.

On keeping irradiated samples of PVC at 77° in air for 24 hr there is a small reduction in the strength of the EPR signal and a peroxide-radical signal appears.

The rate of recombination and oxidation of the radicals increases with increasing temperature.

Further investigation is necessary for the elucidation of the kinetics of these processes.

CONCLUSIONS

The profound changes in the molecular structure of PVC after irradiation with high speed electrons consist mainly in the elimination of HCl and the formation of double bonds.

It may be considered that the colour changes are connected with processes involving the participation of radicals, the presence of which was established by electron paramagnetic resonance. The concentration of radicals decreases with time. *In vacuo* this decrease can evidently be explained by recombination of the radicals and in the presence of atmospheric oxygen by reaction of the free radicals with oxygen to form peroxide radicals. On heating, the rate of disappearance of free radicals increases considerably and at the same time chromophores are formed that increase the colour of the polymer.

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THE POLYMERIZATION OF ETHYLENE BY γ-RADIATION *

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A NUMBER of papers have dealt with the study of the polymerization of ethylene by γ-radiation. It has been shown that at low pressures (up to 20atm) [1] the reaction rate is proportional to the concentration of ethylene to the power of 1 to 1·5. At higher pressures the kinetics of the process become more complex. The polymerization rate increases with time [2, 3] and rises rapidly with the ethylene concentration (in the pressure interval from 450–11,200atm the over all rate of the process is proportional to the ethylene concentration to the power of 10–15 and to the fugacity to the power of 1·3–1·8) [4]. The change in the overall polymerization rate does not obey the Arrhenius equation.

The activation energy in the temperature interval from 20–200°C varies from 3 to 14kcal/mole [4].

The density of radiation-polymerized polyethylene, obtained at room temperature, is 0·93–0·95. This product possesses relatively high crystallinity (crystalline phase content 70–77%) [3, 5, 6]. It has been reported [3, 6] that samples of polyethylene obtained by γ-irradiation have satisfactory tear strength but low fractional elongation (from 4-80 per cent).

As would be expected radiation-polymerized polyethylene differs in its high degree of purity. This is very important in connexion with the problem of producing polyethylene with good dielectric properties [2].

However the data available in the literature do not give a sufficiently complete picture of the polymerization of ethylene by γ-radiation. Isolated information on the kinetic relationships of the radiation polymerization of this monomer has been obtained at low (up to 20atm) [1] or at relatively high pressures (500–1500atm) [4]. Meanwhile there is considerable interest in investigation of the specific features of the radiation polymerization of ethylene in the medium pressure region (100–300atm). Since the rate of radiation initiation does not depend on temperature, polymerization in this case can be carried out at room temperature or even at lower temperatures.

Under these conditions, at pressures of 100–300atm, the concentration of ethylene is sufficient to produce a product of high molecular weight.

* Vysokomol. soedin. **2**: No. 6, 904–915, 1960.

In this work the rate of polymerization of ethylene by γ-radiation was studied in solution and in the gas phase at various ethylene pressures (concentrations) and dose rates. Some relationships between the polymer characteristics and the process conditions were obtained.

METHOD

The polymerizations were carried out with γ-radiation from radioactive ^{60}Co in sources at the Karpov Institute (1400, 18,000 and 20,000 g-equiv of radium [7, 8]) at pressures from 50 to 300 atm, dose rates from 17 to 165 roentgens) sec and a temperature of 25°. Some experiments were carried out at 50°. The ethylene used was obtained from ethyl alcohol, shown by mass-spectrometric analysis* to contain the following impurities (in volumes percent):

TABLE A

Impurity	Experiment No. 1	Experiment No. 2
Propylene	0·087	0·080
Butylene	0·041	0·020
Limit hydrocarbons	1·35	1·47
Oxygen	0·005	0·01

It was found that the polymerization of ethylene containing greater amounts of unsaturated hydrocarbons (up to 2 per cent) and oxygen (up to 0·2 per cent) proceeds at a lower rate.

The reaction vessels, made of stainless, antimagnetic steel, consisted of cylindrical ampoules of 40–50 ml capacity with a screw cap and fitted with a magnetic stirrer, a thermocouple pocket and a thermostatting jacket. For the removal of air, the system was evacuated (to a pressure of 10^{-2} mm) three times and filled with ethylene. The amount of ethylene in the reaction vessel was determined by weighing. For polymerization in solution the solvent was freed from air by freezing and degassing *in vacuo* several times, and was then saturated with ethylene under pressure while stirring with the magnetic stirrer. The yield of polymer at various degrees of conversion was determined by weight.

Polymerization was carried out at constant pressure (ethylene was added during the process) and at falling pressure.

The lay-out of the apparatus for polymerization in solution and in the gas phase with a K-1400 source† is shown in Figure 1.

Experiments were carried out simultaneously in two vessels protected by a lead stopper 1 and placed in a protective chamber 2. The vessels 3 were filled with ethylene from a cylinder§ through a gas tube, with a tap 4, and a manifold.

* The authors thank M. V. Tikhomirova and M. V. Gur'eva for carrying out the mass-spectrometric analysis of the ethylene.

† A discription of the source is given in reference [7].

§ Steel cylinders of 500 ml capacity were used, previously filled with ethylene at the temperature of liquid nitrogen. The pressure in the cylinders at room temperature varied between 300 and 500 atm depending on the experimental conditions.

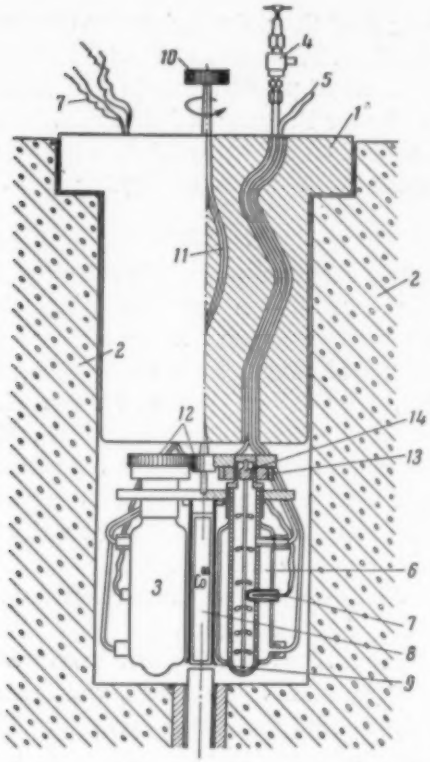

FIG. 1. Diagram of apparatus for polymerization of ethylene with the K-1400 source.

The system was first evacuated to a pressure of 10^{-2}mm (tested by means of a thermocouple vacuum gauge). In order to maintain a constant reaction temperature an ultrathermostat system was used, achieved by circulating water through the tubes 5 and the jackets 6 surrounding the vessels. The temperature was measured by means of thermocouples 7 placed in the pockets in the reaction vessels. The radiation source was introduced in a screened, brass cylinder 9 from a special container in which it is kept when not in use. The stirrer is rotated by transmission from an electric motor through the gear-wheel 10, the flexible shaft 11, the system of gear-wheels 12, the driving magnet 13 and the driven magnet 14.

For setteing up experiments with sources K-18,000 and K-20,000* the vessels were placed in an oil thermostat.

The energy absorbed was determined by chemical dosimetry by the oxidation of divalent iron in glass test-tubes placed in the reaction vessels. For calculation of the energy absorbed it was assumed that 1 roentgen corresponds to 93 ergs per gramme of water.

* The arrangement of the sources is described in reference [8].

The molecular weight of the polyethylene was determined by the method of light scattering* and from the intrinsic viscosities of solutions of the polymers. The viscosities of solutions of polyethylene in tetralin and xylene were determined at 105° and 110° over the range of concentrations from 0·03 to 0·20g/dl in the viscometer described in reference [9]. The density of the polymers was determined by the method of hydrostatic weighing in water-methanol mixtures.

RESULTS

Polymerization of ethylene dissolved in organic solvents. Free radicals that can serve as initiators of polymerization are formed by the action of nuclear radiation on organic compounds. Hence the use of these compounds as solvents or additives provides one of the methods of increasing the effectiveness of radiation polymerization, especially of those monomers which, in the pure state, polymerize slowly because of hindering involved in the initiation reaction. In the polymerization of ethylene an additional positive effect of the solvent is that (in the region of not very high pressures) at the same ethylene pressures its concentration in solution is considerably higher than in the gaseous state. Thus, at a pressure of 50atm and a temperature of 25° the concentration of ethylene in the gas phase is 0·10g/ml. and in solution in various solvents (Table 1) it lies between the limits of 0·17–0·26g/ml.

Experimental polymerizations in solutions were carried out at pressures of 37–50atm and at 25°. In methanol, acetone, cyclohexane and heptane (15ml) the yield of solid polyethylene and the polymerization rate was some 15–25 times greater than in gas-phase polymerizations at the same pressures and temperature (Table 1). The G-values shown in Table 1 are not the optimal values because these experiments were carried out only with relatively high dose rates ($\sim$100 roentgens/sec). Nevertheless the data presented indicate that the yield in relation to the energy absorbed, $G_{C_2H_4}$, is considerably higher in the presence of solvents than in the gas phase at the same pressure. The polyethylene produced in these solvents was a white powder with a density of 0·95, readily soluble in hydrocarbons (for example, tetralin and octane) at 100–110°. The average molecular weight of the polymer was 20,000–40,000.

On irradiation of solutions of ethylene in carbon tetrachloride, low-molecular polymers (telomers) of the following structure, $Cl_3C(C_2H_4)_2Cl$ (60%) and $Cl_2C(C_2H_4)_3Cl$, are formed in good yield. These products, the composition of which can be varied by alteration of the process conditions (for example, by changing the ratio of the components in the initial mixture) are of interest for the synthesis of various organic compounds.

Figures 2 and 3 show the results obtained in the polymerization of ethylene in the gas phase and in hexane (concentration of ethylene in solution, 50 per cent by weight) at 50atm and 25° in relation to time. The reaction rate in the

* Investigations of the light scattering of solutions of polyethylene obtained under various conditions were carried out by I. G. Soboleva and N. V. Makletsova. The detailed results of this work will be published in a separate communication.

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TABLE 1. POLYMERIZATION OF ETHYLENE BY γ-RADIATION FROM RADIOACTIVE ^{60}Co

(DOSE RATE $5{\cdot}7\times10^{15}$ eV/g · sec (98 roentgens/sec)

Solvent (ml.)	Temperature (°C)	Initial pressure (atm)	Mean concentration of ethylene in reaction vessel (g/ml.)	Irradiation time (hr)	Total yield of polymer (g)	Rate of conversion	Dosage		G-value §	Molecular weight	
							eV/g × $\times10^{-20}$	megaroentgens		by light scattering	in tetral at 110° (dl./g)
Without solvent in the gas phase	20	48·7	0·103	52	0·211	0·113	10·9	18·7	110	70	0·05
Heptane (5)*	25	49·7	0·129	36	1·010	0·58	7·53	12·9	550	—	0·08
Methanol (15)	20	50·7	0·260	68	5·19	1·7	14·4	25·0	477	26	0·15
Acetone	20	37·3	0·200	68	2·68	0·56	13·8	23·7	223	—	0·08
Cyclohexane	16	50·5	0·170	39	5·50	2·85	7·3	12·5	800	20	0·18
Heptane (15)	16	42·0	0·170	39	3·40	1·40	8·0	13·7	540	38	0·18
Heptane (5)*	25	49·0	0·122	45·5	1·67	0·74	9·5	16·0	364	—	0·17
Mixture of heptane (15) and benzene (1·5)*	20	51·9	0·175	44	3·60	1·17	5·8	10·0	700	33	0·14
Carbon tetrachloride (15)	20	44·5	0·190	68	5·58+	1·30	12·9	22·0	110	Low-molecular liquid products	

* Volume of reaction vessel 41 ml.; in the other experiments 35 ml.

† The telomers contain 2·01 g of combined ethylene

§ In molecules of ethylene per 100 eV of absorbed energy

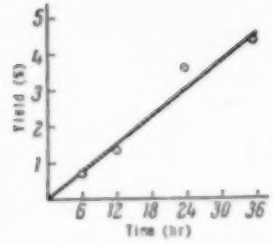

FIG. 2. Polymerization of ethylene in the gas phase. Pressure 50 atm, temperature 25°, dose rate 98 roentgens/sec.

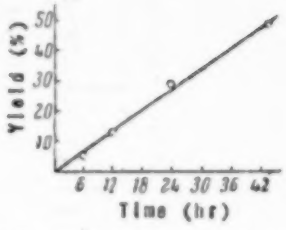

FIG. 3. Polymerization of ethylene in hexane. Pressure 50 atm, ethylene concentration in solution 50% by weight, temperature 25°, dose rate 98 roentgens/sec.

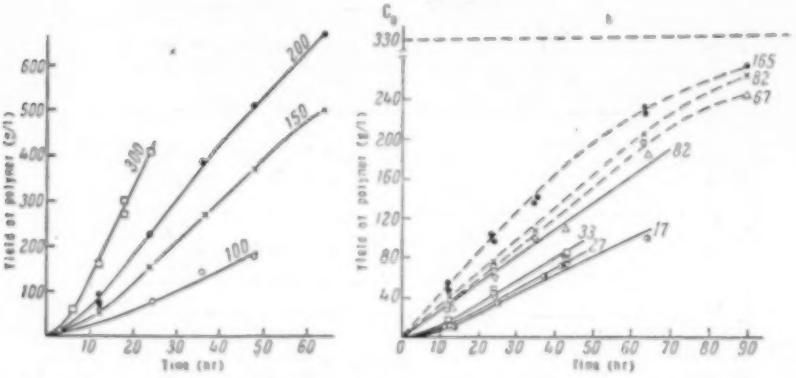

FIG. 4. Dependence of yield of polymer on polymerization time: (a) at different pressures; (b) at different dose rates (the pressures in atmospheres and dose rates in roentgens/sec are shown on the curves). (a) Dose rate 72 roentgens/sec, temperature 25°. The pressure was constant throughout the process; (b) Experiments with Falling Pressure. Initial pressure 100 atm, temperature 25°. Continuous curve, ethylene sample No. 1; dotted curve, ethylene sample No. 2.

gas phase (in the initial stages) and in solution (up to 50 per cent conversion) is approximately directly proprtional to time, the overall polymerization rate in solution being about 10 times greater than in the gas phase. In these experiments the concentration of ethylene in the solution was 0·24–0·26g/ml. and the rate of polymerization was 1·2 per cent per hour. This concentration of ethylene in the gas phase would correspond to a pressure of 70atm. At this pressure the polymerization rate in the gas phase is 0·5 per cent per hour, i.e. at the same ethylene concentration the rate of polymerization in hexane is greater than that in the gas phase by a factor of 2·5. This result is a direct indication of the sensitizing action resulting from the high probability of the formation of radicals from the solvent molecules. It was shown that at ethylene pressures of 50–70atm and concentrations in solution of 0·25–0·30g/ml. at 25° (close to phase equilibrium) the polymers formed are of lower molecular weight than in polymerization in the gas phase at the same concentrations.

Polymerization of ethylene in the gas phase. (1) The variation of reaction rate with time was studied at constant pressure (compensating for the ethylene reacted), and with the pressure falling during the course of the reaction.

Figure 4a shows the variation of the yield of polymer with time at various initial pressures (the pressure was kept constant during the reaction period). The polymerization rate at first increases with time (up to a yield of about 100g/l.) and then (up to a yield of 400g/l.) remains constant. After this the reaction rate decreases a little. The experiments with falling pressure conditions were carried out at initial pressures of 100 and 150 atm and various dose rates. At low dose rates (17–33 roentgens/sec) a small increase in reaction rate at the beginning of the process was again observed, then the polymerization rate was constant with respect to time up to a yield of 150–200g/l. (50–60 per cent) after which the rate decreased as a result of the fall in ethylene concentration(Fig. 4b)

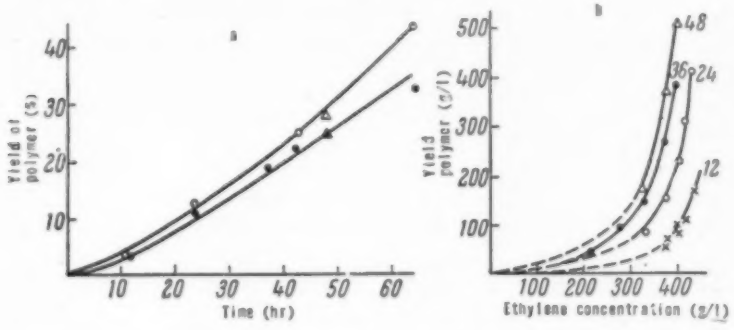

FIG. 5. Dependence of yield of polymer (a) on polymerization time at 100 atm and 25°; (b) on ethylene concentration. (a) O and Δ, experiments at 27 roentgens/sec; ● and ▲, experiments at 17 roentgens/sec; Δ and ▲, experiments in which the ethylene was replaced by a fresh supply after polymerization for 24 hr; (b) polymerization times (hr) shown on curves. Experiments at constant pressure. Dose rate 72 roentgens/sec, temperature 25°.

Experiments were carried out in which unreacted ethylene from the initial charge was replaced by fresh material (after polymerization for 24hr). No change in polymerization rate was observed in these experiments (Fig. 5a). Consequently the observed increase in rate during the early stages of the process (Fig. 4a and b) is evidently not connected with inhibition by impurities (propylene, butylene) which are present in small quantities in the monomer but is due mainly to the effect of the polymer, which forms a new phase.

Thus it was shown that the yield of polymer increases considerably when the reaction takes place in the presence of polyethylene (Table 2). For these experiments polyethylene was first prepared in the reaction vessels, the unreacted ethylene was blown off to the atmosphere and fresh ethylene was passed in to the vessels, avoiding the intake of air.

The average molecular weight of the polymers found by the light scattering method, and the intrinsic viscosity of the polymer solutions increased with

TABLE 2. EFFECT OF ADDITION OF POLYETHYLENE ON THE POLYMERIZATION OF ETHYLENE.

Initial pressure 200 atm (ethylene concentration 0·4 g/ml.). Dose rate 33·3 roentgens/sec. Polymerization time 36 hr.

Initial concentration of polymer (g/ml. of reaction volume*)	Yield of polymer (%)	Initial concentration of polymer (g/ml. of reaction volume*)	Yield of polymer (%)
—	39·5	0·111	55·5
—	41·5	0·145	62·5
0·103	55·5	0·157	58·2
0·097	54·3		

* Total volume of reaction vessel, 45 ml.

TABLE 3. DEPENDENCE OF MOLECULAR WEIGHT AND INTRINSIC VISCOSITY [η] OF POLYETHYLENE ON DEGREE OF CONVERSION.

Initial pressure 100 atm; (experiments with falling pressure); temperature 25°

Irradiation time (hr)	Yield of polymer		Molecular weight by light-scattering $M \times 10^{-3}$	In xylene at 105° (dl./g)
	(%)	g/l.		
		Dose rate 17 roentgens/sec		
12	3·7	11·9	—	0·80
24	10·8	35·2	133	0·84
37	18·3	60·0	200	1·18
64	32·0	101·0	—	2·80
		Dose rate 27 roentgens/sec		
12	3·2	10·2	—	0·40
24	12·4	41·0	125	0·84
43	24·2	78·5	—	1·69
		Dose rate 33 roentgens/sec		
12	5·4	18·1	—	0·70
24	13·9	45·2	150	0·77
		Dose rate 82 roentgens/sec		
12	9·9	32·2	56	0·50
24	18·5	61·0	—	0·52
43	33·8	11·2	—	0·92
		Dose rate 165 roentgens/sec		
12	16·3	54·0	—	0·57
24	14·9	49·0	—	0·95
36	42·3	139·0	—	1·11

the degree of conversion (Table 3). This can be explained by the fact that polymerization is initiated also by radicals formed by radiolysis of the polymer. The branching brought about as a result of this increases the molecular weight of the polymer substantially.

(2) The effect of pressure. The polymerization rate increases sharply on increasing the ethylene concentration. This is seen from Figure 5b, on which is shown the dependence of the yield of polymer on the ethylene concentration at various reaction times, and also at various ethylene pressures, and from Figure 4a which illustrates the dependence of the yield of polymer on time. Since the rate of polymerization increases during the early stages of the reaction (Fig. 4a) the mean rate (at a given time) and the maximal rate of polymerization were determined, as characteristics of the process. The maximal rate was calculated from the slope of the straight-line portion of the curves of yield against time.

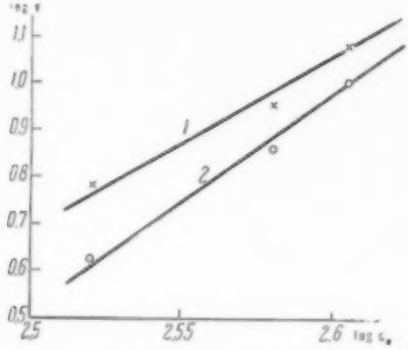

FIG. 6. Dependence of the logarithm of the maximal (1) and average (over 36 hr) (2) polymerization rate on the logarithm of the ethylene concentration (C_0). Experiments at constant pressure. Dose rate 72 roentgens/sec, temperature 25°.

TABLE 4. DEPENDENCE OF THE RATE OF POLYMERIZATION OF ETHYLENE (V) AND G-VALUE (G) ON PRESSURE (OR ON CONCENTRATION C_0)

(Experiments at constant ethylene pressure, temperature 25°, dose rate 72 roentgens/sec)

	Pressure (atm)			
	100 (C_0 = 330 g/l.)	150 (C_0 = 380 g/l.)	200 (C_0 = 402 g/l.)	300 (C_0 = 437 g/l.)
V after 24 hr (g/l.hr)	3·20	6·25	9·30	16·9
V after 36 hr (g/l.hr)	3·88	7·35	10·55	—
V_{max} (g/l.hr)	6·00	9·50	12·80	20·5
G after 24 hr	1200	1900	2500	4300
G after 36 hr	1300	2000	2600	—
G_{max}	2500	3500	4400	6500

Table 4 shows that at 300 atm the mean rate of the process (over 24 hr) is 16·9 g/l. and in the straight-line section of the curves (maximal rate) it is 20·5 g/l. The value of G also rises sharply with increasing ethylene concentration.

In the pressure region studied, the increase in reaction rate and G-value at 25° is proportional to the ethylene concentration to the power of 4–5 (Fig. 6)

or to the fugacity* of the ethylene to the power of 2·5. This unusual dependence of rate on concentration (and on fugacity) may be connected with the sharp change in volume on formation of the active complex in the propagation reaction and also with specific features of the heterogeneous polymerization of ethylene (formation of polymer in the form of a new phase).

The average molecular weight and intrinsic viscosity of the polymers obtained at constant reaction time also increase with increasing ethylene pressure (Table. 5).

TABLE 5. EFFECT OF ETHYLENE PRESSURE ON THE AVERAGE MOLECULAR WEIGHT OF POLYETHYLENE AND ON THE INTRINSIC VISCOSITY OF ITS SOLUTIONS

(Experiments at constant pressure and intensity 72 rentgens/sec, temperature 25°)

Pressure (atm)	Initial concentration (g/l.)	Polymerization time (hr)	Yidld of polymer (g/l.)	[η] in xylol at 105° (dl./g)	$M \times 10^{-3}$ by light scattering
100	330	24	76·6	0·96	190
100	330	36	139·3	Incompletely soluble	
150	380	12	57·2	1·78	230
150	380	24	150	2·13	—
150	380	36	264	Incompletely soluble	
200	402	12	71·8	1·66	280
200	402	24	223	3·52	—
200	402	36	380	Incompletely soluble	
250	420	6	52·1	1·62	—
250	420	24	318	Incompletely soluble (22% dissolves)	
300	437	6	59·4	1·97	—
300	437	12	162	4·05	—
300	437	18	285	Incompletely soluble (27% dissolves)	

(3) The effect of dose rate was studied at initial pressures of 100 and 150 atm with falling pressure during the course of the reaction, over the range of dose rates from 17 to 165 roentgens/sec. It is seen from Fig. 7 that the maximal reaction rate increases to some extent with increasing dose rate. This rate is proportional to the dose rate to the power of 0·3. The G-value (Fig. 8) falls sharply with increasing dose rate ($G = KI^{-0.7}$).

The observed dependence of rate of polymerization V on dose rate can be explained by the fact that in addition to chain termination by the interaction of two polymeric radicals, because of the low mobility of the polymeric radicals in solid polyethylene; termination also takes place by the interaction of poly-

* The values of the fugacity of the ethylene were taken partly from reference [10] and the intermediate values were calculated by the method of corresponding states [11].

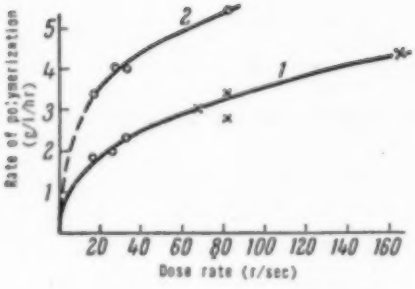

FIG. 7. Dependence of the maximal rate on dose rate at initial pressures of 100 atm (1) and 150 atm (2). Experiments with falling pressure at 25°. Circles, ethylene sample No. 1; crosses, ethylene sample No. 2.

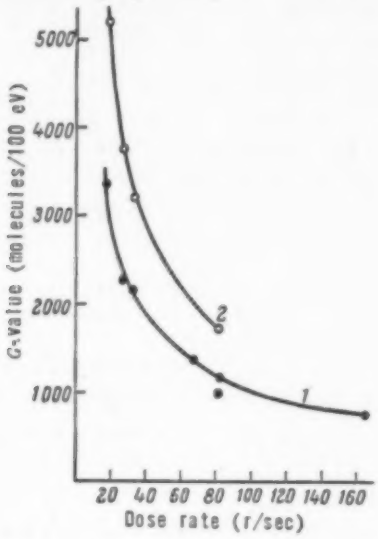

FIG. 8. Dependence of the maximal G-value on dose rate at initial pressures of 100 atm (1) and 150 atm (2). Experiments with falling pressure at 25°.

meric radicals with primary radicals which in the limit leads to the independence of V on I. The extent to which the second reaction occurs increases with increasing concentration of primary radicals. The molecular weight of the polyethylene increases with decreasing dose rate (Table 6).

(4) The effect of temperature was investigated at dose rates from 17 to 82 roentgens/sec. An increase in temperature from 25° to 50° at a constant initial concentration of ethylene of 330g/l. (corresponding to a pressure of 100atm at 25° and 175atm at 50°) resulted, as would be expected, in a small increase in polymerization rate and in the molecular weight of the polymer (Table 7). The

TABLE 6. THE EFFECT OF DOSE RATE (*I*) ON MOLECULAR WEIGHT (M) OF POLYTHENE

Experiments with falling pressure at 25°. Initial pressure 150 atm, polymerization time 12 hr.

I (roentgens/sec)	Yield of polymer (g/l.)	Mean rate (g/l./hr)	$[\eta]$ in xylene at 105° (dl./g)	$M \times 10^{-3}$ by light scattering
17	27·0	2·25	1·80	330
27	44·0	3·67	1·50	250
33	47·5	3·96	1·55	286
82	56·0	4·67	0·90	125

TABLE 7. THE EFFECT OF TEMPERATURE ON POLYMERIZATION RATE (V_{max}), G-VALUE (G_{max}) AND MOLECULAR WEIGHT (M) OF THE POLYMERS AT VARIOUS DOSE RATES.

(Experiments with falling pressure)

Dose rate (roentgens/sec)	25°				50°				
	V_{max} (g/l./hr)	G_{max}	$[\eta]$	M × 10^{-3}	V_{max} (g/l./hr)	G_{max}	$[\eta]$	M × 10^{-3}	E (kcal/mole)
17	1·85	2300	0·8	—	2·3	4100	1·29	435	1·7
27	2·00	2300	0·4	—	2·7	3000	1·30	540	2·3
33	2·30	2100	0·7	48	2·8	2600	1·43	800	1·5
82	2·72	1000	0·5	56	3·8	1400	0·71	230	2·6

increase in rate on raising the temperature from 25° to 50° corresponds to an overall activation energy of 1·5–2·5 kcal/mole.

It is seen from Tables 5–7 that the relationship between the intrinsic viscosity and molecular weight of the polymers depends on the polymerization temperature. Polymers obtained at 50°, with viscosity values close to those of polymers obtained at 25°, have considerably higher molecular weights. This indicates that with increase in polymerization temperature branching of the polymers obtained increases.

Properties of radiation polyethylene. The density of the samples of polyethylene obtained, measured by the method of hydrostatic weighing, varied between the limits of 0·945 to 0·975 g/cm³.

The crystallinity of the polyethylene was estimated from X-ray diffraction patterns. It was found that the crystallinity of radiation polyethylene is higher than that of high-pressure polyethylene.

The mechanical properties of radiation polyethylene were studied in relation to the conditions of preparation.* The results of these investigations showed that these properties are much improved when the process is carried out at pressures above 100 atm. Polymers prepared in the pressure range from 250–300 atm have a breaking strength of 210–240 kg/cm² and an elongation at break of 200–400 per cent.

The authors express their gratitude to A. Kh. Breger, V. B. Osipov and V. A. Gol'din for assistance in the organization and setting up of experiments with the radiation sources.

CONCLUSIONS

The radiation induced polymerization of ethylene in the gas phase and in organic solvents, and also some properties of the polymers formed, have been studied. I. Polymerization in heptane, cyclohexane, methanol and acetone was

* Investigation of the crystallinity and mechanical properties of the polyethylene was carried out in the Radiation Chemistry of Polymers Laboratory at the L. Ya. Karpov Institute by Yu. M. Malinskii and B. I. Zverev. The results obtained will be discussed in detail elsewhere.

studied at a pressure of 50atm, a temperature of 25° and a dose rate of 98 roentgens/sec. Under these conditions the reaction proceeds at a rate 10 times greater than that in the gas phase at the same pressure. The polymers formed have average molecular weights of 20,000–40,000. In carbon tetrachloride tetrachloroalkanes (telomers) of different molecular weights are formed in high yield II. Polymerization in the gas phase was studied at constant and falling pressures. At constant pressure—in the region from 100 to 300atm at a dose rate of 72 roentgens/sec, and at falling pressure—over the range of dose rates from 17 to 165 roentgens/sec, pressures of 100 and 150atm and temperatures of 25° and 50°.

(1) The polymerization rate increases with time at low degrees of conversion and then becomes constant. At high conversion the polymerization rate decreases. The average molecular weight and intrinsic viscosity of the polymers increases with the degree of conversion. The reaction rate in the straight-line section of the curves of yield of polymer against time (maximal rate) is proportional to the ethylene concentration to the power of 4–5.

(2) The mean reaction rate (polymerization time, 24hr) at a pressure of 300atm, at temperature of 25° and a dose rate of 72 roentgens/sec is 16·9g/l.hr. The maximal rate is 20·5g/l.hr. The G-values under these conditions are respectively 4300 and 6500 molecules of ethylene per 100eV of absorbed energy. On increasing the pressure from 100 to 300atm the intrinsic viscosity of the polymers increases from 1 to 4 (in the early stages of the process).

(3) The reaction rate is proportional to the dose rate to the power of 0·3. The G-value is inversely proportional to the dose rate to the power of 0.7 and its value at an initial pressure of 150atm and a dose rate of 17 roentgens/sec is about 5000 molecules per 100eV. The molecular weight of the polyethylene increases with decreasing dose rate.

(4) An increase in temperature from 25° to 50° at constant ethylene concentration (330g/l.) results in a small increase in polymerization rate and in molecular weight.

(5) The polyethylene obtained has higher density (0·945–0·975g/cm^3) and crystallinity than high-pressure polyethylene.

(6) The relationships found between the polymerization rate and time, ethylene concentration and dose rate can be examined quantitatively only after a detailed study of the special features of the process relating to its heterogeneous nature.

Translated by E. O. PHILLIPS

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THE POLYCONDENSATION OF SOME 4,4′-DIALKYLAMINO-3,3′-DIMETHYLDIPHENYLMETHANES WITH SEBACIC ACID*

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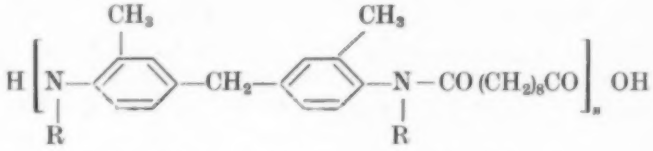
IN continuation of investigations published previously on the synthesis of polyamides from primary and secondary diamines of the diarylmethane series with adipic acid [1, 2], this paper deals with the synthesis and properties of new polymers of the same series from N,N′-diethyl, dipropyl and dibutyl derivatives of 4,4′-diamino-3,3′-dimethyldiphenylmethane and sebacic acid.

From the polycondensation of the above substituted diamines with sebacic acid we obtained three polyamides: poly-3,3′-dimethyldiphenylmethane-N,N′-diethylsebacamide (I), poly-3,3′-dimethyldiphenylmethane-N,N′-dipropylsebacamide (II) and poly-3,3′-dimethyldiphenylmethane-N,N′-dibutylsebacamide (III), of the general formula



(where $R = C_2H_5$, C_3H_7, C_4H_9), which was established by determination of the end groups.

The polyamides obtained are transparent, slightly yellow, glass-like products readily soluble in alcohol, benzene, acetone and other solvents, and have good adhesion to various materials such as metal, glass, fabrics and wood. The specific viscosity of 0·5 per cent solutions of the polyamides was 0·4–0·5 and the molecular weight by end-group analysis was 2700–3100 and by the viscometric method, 3000–4000. The molecular weights are dependent on the size of the alkyl group attached to the nitrogen atom and the low values are explained by steric hindrance in the polycondensation process. Turbidimetric titration showed that these polyamides are more polydisperse in molecular weight than the polyamides from primary diamines (Fig. 1). However the fairly close agreement between the molecular weights found by the viscometric and chemical methods shows that the polydispersity is relatively low. The falling-drop temperatures, determined in the Ubbelohde apparatus, also vary with the number

* Vysokomol. soedin. **2**: No. 6, 952–956, 1960.

of carbon atoms in the substituent on the nitrogen atom and were respectively (I) 90°, II 68° and (III) 65°C. The capillary-tube melting points were 63–65°-56–58° and 52–54°C respectively.

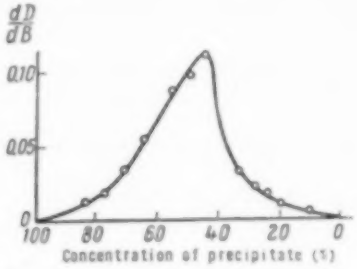


FIG. 1. Differential curve characterizing the polydispersity of the polymer.

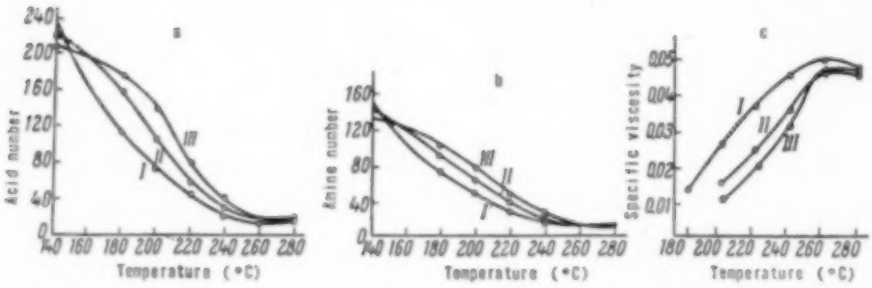


FIG. 2. Relative reactivity of the diamines, measured by (a) the dependence of the acid number of the reaction mixture on temperature; (b) the dependence of amine number on temperature; (c) the dependence of the specific viscosity of the polymer on temperature.

From a study of the reaction conditions, for the purpose of obtaining polymers of higher molecular weight, it was found that the reactivity of the diamines decreases with increasing number of carbon atoms in the group attached to the nitrogen atom. However this difference in reactivity practically disappears at 260° (Fig. 2, a, b and c), which is the optimal temperature. Polymers of highest molecular weight are obtained at 260°; at 280° and above the molecular weight falls.

It is known that aromatic diamines do not form salts with dicarboxylic acids. As a result of the volatility of one of the components (most often the diamine) the ratio of the starting materials is altered. It has been found [1] that in the synthesis of polyamides from aromatic diamines and dicarboxylic acids it is profitable to add a small excess of the diamine.

In this case also it was found that for the purpose of obtaining a polymer of higher molecular weight it was effective to add 1–2 per cent excess diamine, though the difference in molecular weight was not great.

The kinetics of the reaction at 260° were studied, taking the reaction with 4,4′-diethylamino-3,3′-dimethyldiphenylmethane as an example. It was found

that in the early stages of condensation the products are thick, viscous liquids, gradually changing to solid, brittle, glassy materials. Polymer formation was practically complete in 3–4 hr (Fig. 4).

The results reported in this and previous papers enable some general observations to be made on the synthesis and properties of poly-3,3′-dimethylphenyl-

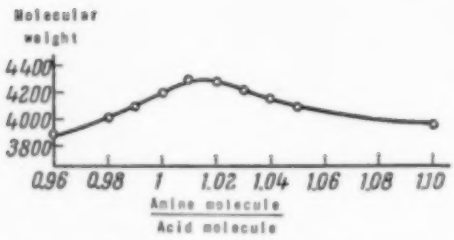


FIG. 3. Dependence of the molecular weight of the polyamides on the ratio of the starting materials.

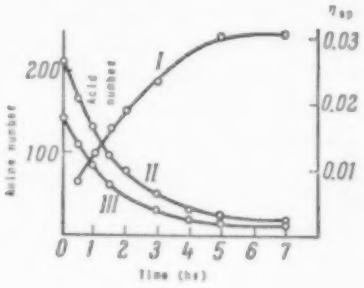
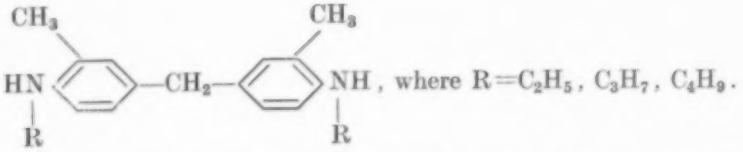


FIG. 4. Dependence of the acid and amine numbers and specific viscosity on the time of polycondensation of 4,4′-diethylamino-3,3′-dimethyldiphenylmethane with sebacic acid.

methane-N,N′-dialkylsebacamides obtained from sebacic acid and diamines of the general formula



, where $R = C_2H_5$, C_3H_7, C_4H_9.

These diamines are very different in reactivity because with increasing size of the substituent on the nitrogen atom the steric hindrance to the reaction increases considerably. The larger the substituent R the lower the degree of polycondensation at any moment from the start of the process, though on carrying out the reaction at 260° the abolute values of the molecular weight of (II) and (III) are very close (2810 and 2950 respectively).

In addition to the substantial effect on the process of polycondensation the structure of the diamines used determines the properties of the polyamides to a considerable extent. Their solubility melting point, external form and other properties are connected with the magnitude of the intermolecular forces an the packing density of the polymer chains. For example, the molecules of poly-3,3′-dimethyldiphenylmethanesebacamide are strongly linked by hydrogen bonds, as a result of which the polymer is insoluble in the usual organic solvents. For the same reason this polymer has a high melting point (248°). Finally the opacity, porcelain-like appearance and conchoidal fracture, which are characteristic of this polymer, are phenomena inherent only in highly ordered structures.

In the molecules of the polyamides obtained from N,N′-substituted diamines the number of intermolecular bonds falls sharply, and consequently they are glass-like, readily soluble and low melting. On passing from the unsubstituted polyamide to the ethyl derivative a sharp fall in melting point is observed, which is a result of the disappearance of hydrogen bonds. Further increase in the number of carbon atoms in the substituent on the nitrogen atom causes a very small decrease in melting point, brought about by the looser packing of the polymer chains. An interesting feature is the fact that the melting points of these polymers are close to those of the corresponding series of polymers from the same diamines and adipic acid [1, 2]. This obviously can be explained by the fact that in the series of N-substituted polyamides, where hydrogen bonding is absent, the melting point depends, as in the case of carbon-chain polymers, mainly on molecular weight and the presence of side chains and their size.

EXPERIMENTAL

For carrying out the polycondensations a mixture of equimolecular quantities of diamine and sebacic acid was placed in a three-necked flask or special reaction tube with an outlet, and heated on a Wood's metal bath. The reaction was carried out initially at normal pressure in an atmosphere of inert gas (carbon dioxide) for 5hr, then heating was continued for 2 hr *in vacuo*. The effect of reaction time was followed by taking samples at intervals and determining the acid number, the amine number in non aqueous solutions and the specific viscosity of 0·5 per cent solutions in alcohol. Molecular weights were determined chemically, by end-group analysis, and viscometrically. In the latter case tha calculation was made according to the formula $\eta_{sp}/c = KM$, where $K = 11 \times 10^{-4}$ (found for methanol solutions of polyamides of this series [1]) and by Korshak and Pavlova's equation [3] for polyamides in methanol solution, $\eta/c = 3{\cdot}9 \times 10^{-6} M^{0{\cdot}96}$ at $c = 5$ g/l. The molecular weights calculated according to the two equations were in fairly good agreement. For example, in the determination of the dependence of molecular weight on reaction time at 260° in the system N,N-diethyl-substituted diamine–sebacic acid the following results were obtained (see Table 1).

Table 1. Molecular weight of polyamides

Reaction time (hr)	Mol. wt. according to [1]	Mol. wt. according to [3]	Reaction time (hr)	Mol. wt. according to [1]	Mol. wt. according to [3]
0·5	790	800	3	1910	1790
1	1120	1070	4	2220	2200
1·5	1350	1290	5	2550	2560
2	1560	1520	7	2570	2580

The polydispersity of the polymers was determined by turbidometric titration. The polymer was precipitated from dilute solution (0·01 per cent in acetone) by addition of a precipitant (distilled water). The light absorbed by the suspension

formed was measured and the calculation was made according to the formula $I/I_0=f(v)$, where I_0 is the initial intensity of the light after passing through the cell filled with the solution, I is the intensity after formation of the suspension and v is the concentration of the precipitant. By plotting D (the optical density) against B (the percentage concentration of precipitant) the integral curve was constructed and by differentiating with respect to B the differential distribution curve was obtained.

CONCLUSIONS

(1) Poly-3,3′-dimethyldiphenylmethane-N,N′-dimethyl'dipropyl- and -dibutyl-sebacamides have been synthesized and described for the first time.

(1) The polycondensation conditions and the relative reactivities of the diamines in relation to the number of carbon atoms in the substituent on the nitrogen atom have been studied.

(3) A comparison is given of the properties of the polyamides obtained, in relation to the size of the radical on the nitrogen atom, and also to the disappearance of hydrogen bonds. In particular it was found that the variation of melting point was unusual for polyamides, depending not on the number of carbon atoms in the acid component but mainly on molecular weight and the presence and size of side groups.

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2. **O. Ya. FEDOTOVA, J. P. LOSEV, M. A. ASKAROV** and **P. G. KOSTINA,** Zh. obshch. khim. **29**: 672, 1959
3. **V. V. KORSHAK** and **S. A. PAVLOVA,** Izv. Akad. Nauk SSSR, otd. khim. nauk 1107, 1955

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ABSTRACTS FROM PAPERS PUBLISHED IN

*VYSOKOMOLEKULIARNYE SOEDINENIIA**†

INTERFACIAL POLYCONDENSATION OF DIAMINE SALTS AND DICARBOXYLIC ACID CHLORIDES

L. B. Sokolov and T. V. Kudim, Vysokomol. soedin. **2**: No. 4, 481–484, 1960.

THE possibility of interfacial polycondensation between dicarboxylic acid chlorides and the salts of diamines with strong acids has been demonstrated on the example of terephthalyl chloride and the hydrochlorides of ethylenediamine and hexamethylenediamine. It has been found that the yield and molecular weight of the polymer formed depend upon the alkali concentration in the aqueous phase.

THE MECHANICAL PROPERTIES OF INORGANIC GLASSES IN THE ANOMALY REGION AND THEIR STRUCTURE

G. M. Bartenev and A. S. Eremeeva, Vysokomol. seodin. **2**: No. 4, 508–513, 1960.

IN inorganic glasses above the softening point (500–700°C) and at low stresses (below the yield value) deformations take place similar to the high elasticity deformations of amorphous polymers (thermomechanical curves, spontaneous deformation of specimens with frozen stresses, etc.) The broken-down structure is partially recovered on holding the glass in the anomaly region (thixotropic properties).

These properties of the inorganic glasses relate their structure both to polymer glasses and to structurized colloid systems. A number of glasses possess a clearly defined disperse structure (microheterogeneous glasses). However, the high elastic and thixotropic properties are weakly manifested in inorganic glasses because the yield value, connected with the strength of their structural lattice, is very low. Hence in the anomaly region these material at loads above 1 kg/cm² behave as high viscous liquids.

REVERSION IN THE VULCANIZATION OF RUBBER BY TETRAMETHYLTHIURAMDISULPHIDE

B. A. Dogadkin, V. A. Shershnev and A. T. Dobramislova, Vysokomol. soedin. **2**: No. 4, 513–517, 1960.

REVERSION in the vulcanization of natural rubber and synthetic isoprene rubber mixed with tetramethylthiuramdisulphide (TMTD) takes place in the absence of a metallic oxide or in the presence of magnesium and calcium oxides but not in the presence of zinc oxide. If all the mixes are prepared in an argon atmosphere and are vulcanized in a press, reversion phenomena are not observed. The amount of TMTD bound with the rubber and of the volatiles evolved is the same whether the mixes are prepared in air or in argon. In the presence of zinc oxide dimethyldithiocarbamic acid becomes bound in the form of the zinc salt, an anti-ageing agent, which is the reason for the absence of reversion. Reversion in

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rubber vulcanization with TMTD is due to oxidative degradation processes that are intensified by decomposition products of dimenthyldithiocarbamic acid (carbon bisulphide and dimethylamine).

POLYMERS ON THE BASIS OF 4,4′-DIHYDROXYDIPHENYLPROPANE AND PHTHALIC ACIDS

K. A. Andrianov, I. L. Parbuzina and N. N. Sokolov, Vysokomol. soedin. **2**: No. 4, 518–520, 1960.

THE condensation of 4,4′-dihydroxydiphenylpropane with phthalic and with isophthalic acids, and with dimethyl terephthalate has been investigated. The melting point of the resulting polymers has been found to depend upon the phthalic acid structure.

INVESTIGATION OF THE POLYCONDENSATION OF POLYETHYLENETEREPHTHALATE AND POLYORGANOETHOXYSILOXANES

K. A. Andrianov, O. I. Gribanova, A. G. Prelkova, N. N. Sokolov and Sun Chu-men, Vysokomol. seodin. **2**: No. 4, 521–525, 1960.

THE polycondensation of polyethyleneterephthalate and polymethylphenylethoxysiloxanes has been investigated. It has been found that this reaction leads to polymers with satisfactory mechanical and dielectric properties. A study of the thermal stability of the polymer showed it to be at a high level.

SYNTHESIS OF POLYMERS ON THE BASIS OF β-CHLOROVINYLKETONES

A. N. Nesmeianov, M. I. Rybinskaia and G. I. Slonimskii, Vysokomol. soedin. **2**: No. 4, 526–528, 1960.

A METHOD of synthesizing chelate polymers of the possible structure on the basis

$$\left(\begin{array}{c} -C=C- \\ | \\ COCH_3 \end{array}\right)_n$$

of β-chlorovinylketones has been developed. The polymers formed are rather stable towards the action of high temperatures, non-melting and insoluble. ER spectra, magnetic susceptibility and specific resistance measurements have shown them to possess unusual magnetic and electrical properties.

POLYMERIZATION OF ISOPRENE BY ORGANOMAGNESIUM COMPOUNDS

Wang Fo-shung, B. A. Dolgoplosk and B. L. Erusalimskii, Vysokomol. soedin. **2**: No. 4, 541–545, 1960.

ORGANOMAGNESIUM compounds of the type RMgX and R_2Mg free of ether induce the polymerization od isoprene at 80–90°C. The polyisoprene obtained under such conditions is composed almost entirely of 3,4-links. It is characterized by reduced degree of unsaturation while preserving complete solubility in benzene. The nature of the halogen in the organomagnesium compound does not influence the microstructure of the polymer chain. Complexing agents (diethyl ether and triethylamine) lower the polymerization rate and

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the 3,4-links content. The glass temperature of the polymers is ca. −10°, the intrinsic viscosity 0·75–0·95.

THE GRAFTING OF VARIOUS MONOMERS ONTO POLYVINYLALCOHOL FILMS BY THE ACTION OF X-RADIATION

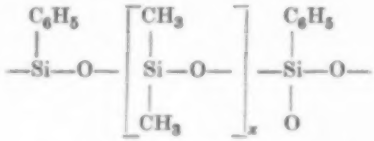
I. Santo and K. Gal, Vysokomol. soedin. **2**: No. 4, 546–548, 1960.

THE grafting of methylmethacrylate (MMA) onto polyvinylalcohol films (PVA) at low radiation doses (4×10^4 roentgens) has been investigated. In the case of MMA the concentration of methyl alcohol used as solvent was found to exert a strong influence upon the extent of grafting. An optimal methanol concentration was found at which already low irradiation doses lead to sharp increase in the extent of grafting.

POLYDIMETHYLPOLYPHENYLSILOXANES

K. A. Andrianov and Sun Chu-men, Vysokomol. soedin. **2**: No. 4, 554–557, 1960.

ON condensation of polydimethylethoxysilanes with phenyltrichlorosilane polydimethylpolyphenysiloxanes of the general formula



with varying distances between the trifunctional groups in the principal chain of the molecule have been obtained.

The properties of the polymers have been investigated and it has been found that with increasing distance between the trifunctional phenylsiloxane groups in the principal chain the thermal stability of the molecules diminishes.

MERCURATED RUBBERS—I. MERCURATED BUTADIENE RUBBERS

R. N. Smirnov, Vysokomol. soedin. **2**: No. 4, 558–562, 1960.

THE mercuration of four butadiene rubbers has been investigated. A procedure for carrying out the reaction both homogeneously and heterogeneously has been proposed which leads to compounds of the type (rubber) OR-Hg $OCOOH_3$. Mercuration not only of the double bonds but also of the methylene groups has been observed. Transition of the rubbers from the amorphous to the crystalline state on mercuration has been noted. Mercurated butadiene rubbers have been found to be of low thermal stability, to electrify on friction, to be easily subject to mechano-chemical processes, to be electrical conductors and to exhibit a sharp decrease in elasticity.

CARBOCHAIN POLYMERS AND COPOLYMERS—XXII. METHACRYLLYLTRIETHYLGERMANIUM, SYNTHESIS AND POLYMERIZATION

H. S. Kolesnikov, S. L. Davydova and N. V. Klimentova, Vysokomol. sedin. **2**: No. 4, 563–566, 1960.

METHACRYLYLTRIETHYLGERMANIUM has been synthesized for the first time and its polymer and styrene and methylmethacrylate copolymers have been obtained. The thermomechanical properties of the polymers have been determined.

CARBOCHAIN POLYMERS AND COPOLYMERS—XXII. COPOLYMERIZATION OF THE DIALLYL DERIVATIVES OF GERMANIUM, TIN AND SILICON WITH STYRENE AND METHYLMETHACRYLATE IN THE PRESENCE OF BENZOYL PEROXIDE

H. S. Kolesnikov, S. L. Davydova, T. I. Ermolaeva, N. D. Shilova and M. B. Bykhovskaya, Vysokomol. soedin. **2**: No. 4, 567–571, 1960.

THE copolymers of the diallyl derivatives of germanium, tin and silicon with styrene and methylmethacrylate have been synthesized and their properties investigated. It has been shown that increase in the organoelement compound in the initial monomer mixture leads to a fall in molecular weight of the copolymers.

INVESTIGATION OF LIGHT SCATTERING IN SILOXANE SOLUTIONS

V. S. Skazka and L. G. Shaltyko, Vysokomol. soedin. **2**: No. 4, 572–575, 1960.

A STUDY has been made of light scattering in toluene solutions of polydimethylsiloxane of molecular weights ranging from $0{\cdot}22\times10^6$ to $4{\cdot}6\times10^6$ and in chlorobenzene solutions of polymethylphenylsiloxane of molecular weights from $0{\cdot}12\times10^6$ to $2{\cdot}2\times10^6$. The same relation between the intrinsic vixcosity $[\eta]$ and molecular weight M_w $[\eta]=3{\cdot}0\times10^{-4}\times M_w$ has been found for both rubbers. The siloxane chain has been shown to possess greater flexibility than the carbon chain. The presence of up to 10% phenyl side groups in the chain has no noticeable effect on its flexibility.

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NEW VINYL ETHER POLYMERS

A. V. Bogdanova, Vysokomol. soedin. **2**: No. 4, 576–580, 1960.

THE polymerization of vinyl-*n*-butyl, vinyl iso-butyl vinyl isopropyl, vinyl cylcohexyl and vinyl β-decalyl ethers in the presence of catalysts prepared from $TiCl_4$ and $Al(C_2H_5)_3$ has been carried out in toluene solution at 75—78°. The isolated polymers have been characterized by their viscosities, solubilities and thermomechanical curves.

A comparative evaluation of the properties of the polymers showed that they differ from the vinyl ethers known up to the present time, apparently because of the regularity of their structure.

THE EFFECT OF STRETCHING ON THE STRUCTURE AND PROPERTIES OF POLYETHYLENETEREPHTHALATE FILMS—I. UNIAXIAL STRETCHING OF THE FILMS

P. V. Kozlov and G. L. Berestneva, Vysokomol. soedin. **2**: No. 4, 590–600, 1960.

THE mechanical properties and structural changes of polyethyleneterephthalate films subjected to uniaxial stretching over a broad range of temperatures at varying rates and up to various limits have been investigated. Orientation, relaxation and crystallization processes taking place in the films being stretched under the various conditions have been examined. At temperatures up to the softening (glass) region the strength characteristics of polyethyleneterephthalate films are determined by orientation processes. Above the softening region all three types of processes take place, a high rate of stretching determining to a large extent the predominant part played by orientation processes up to comparatively high stretching temperatures, permitting transparent films with high strength properties to be obtained under such conditions. It has been shown that on stretching the films above the softening range the crystallization processes lead to two consecutive forms of the crystalline state:

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crystallization in primary structures with the formation of strong transparent films and subsequent spherulite crystallization giving rise to opaque films and to an abrupt fall in strength. On increasing the rate of stretching the temperature region within which microspherulite structures appear shifts considerably in the direction of higher temperatures.

THE EFFECT OF STRETCHING ON THE STRUCTURE AND PROPERTIES OF POLYETHYLENETEREPHTHALATE FILMS—II. TWO-DIMENSIONAL STRETCHING OF THE FILMS

G. L. Berestneva and P. V. Kozlov, Vysokomol. soedin. **2**: No. 4, 601–606, 1960.

THE mechanical properties and structure of polyethyleneterephthalate films subjected to two-dimensional stretching at various rates and over a vide range of temperatures have been investigated. An increase in the stretching rate has been shown to shift the maximum strengths of the films in the direction of elevated stretching temperatures.

The structure of the planar-oriented films has been investigated and it has been found that they are amorphous. However additional heat treatment of the films under stress at temperatures approaching the optimum crystallization of polyterephtalate (170°C) leads to phase transition in the primary structural elements of the films without loss of transparency. Phase transitions in the primary structures of polyterephthalate films both during uniaxial and two-dimensional stretching have been discussed from the standpoint of the packet theory of polymer structure advanced by Kargin, Kitaigorodskii and Slonimskii.

THE ACTION OF ULTRASONIC WAVES ON SYNTHETIC POLYMERS (ANID G-669)

I. E. Elpiner and N. I. Pyshkina, Vysokomol. soedin. **2**: No. 4, 607–613, 1960.

THE polyamide anid G-669 in pure ethanol does not undergo depolymerization by ultrasonic waves, whatever the gas used for saturating the irradiated solutions (air, hydrogen, helium or argon). The same holds true for the polymer dissolved in a mixture of ethand and water (3:1) (in the case of air, helium or argon). On irradiation in the presence of hydrogen the molecular weight of the polymer increases. the intrinsic viscosity falls, pointing to increased branching of the irradiated molecules. In the presence of hydrogen, compressibility of anid G-669 molecules dissolved in ethanol-water mixture of 3:1 ratio, as calculated from data on the velocity of ultrasonic waves in the given liquid, increases. This also is evidence of the branching of anid G-669 irradiated in the presence of hydrogen. It is suggested that these changes are due to activation of the hydrogen and water molecules taking place in the ultrasonic field.

SYNTHESIS OF NEW CELLULOSE AND OTHER POLYSACCHARIDE DERIVATIVES—VIII. SYNTHESIS OF CELLULOSE DIALDEHYDE DIOXIMES AND A STUDY OF THE POSSIBILITY OF THEIR SUBSEQUENT REDUCTION

Yu. S. Kozlova and Z. A. Rogovin, Vysokomol. soedin. **2**: No. 4, 614–618, 1960.

A NEW type of cellulose derivatives, cellulose dialdehyde dioxime, has been synthesized and the stability of these compounds towards various agents has been investigated.

The possibility of synthesizing cellulose diamines by reduction of the dioximes has been tentatively explored using a number of different reducing agents (sodium amalgam, lithium alumohydride and sodium borohydride). By such treatment up to 25% of the total oximide groups cuold be reduced. The maximum amino group content in the reduced product corresponded to a value of $y=15$-18.

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THE APPLICATION OF NITROGEN OXIDES IN THE PREPARATION OF MODIFIED CELLULOSES

J. N. Ermolenko and F. N. Kaputskii, Vysokomol. soedin. **2**: No. 4. 626, 1960.

FOR the preparation of modified cellulose a method incorporating reactive macroradicals into the macromolecule has been proposed, in which the distinguishing feature is the use of nitrogen peroxide. At temperature 0–10°C phosphorus-containing fireproof products have been obtained.

ASYMMETRY OF THE CRITICAL OPALESCENCE IN POLYMER SOLUTIONS

V. S. Skazka, V. N. Tsvetkov and V. E. Eskin, Vysokomol. soedin. **2**: No. 4, 627–628, 1960.

ASYMMETRY of the critical opalescence in polybutylmethacrylate-isopropanol and polystyrene-cyclohexane systems has been revealed. The sizes of the macromolecular coils calculated from the asymmetry data on the basis of Debye's theory are of the order of magnitude of those determined from the molecular weights of the specimens.

ON HETEROCHIAN POLYAMIDES—XXIII. INTERFACE POLYCONDENSATION OF OXY-BIS(*p*-CARBOXYPHENYL) PHENYLPHOSPHINYL DICHLORIDE WITH HEXAMETHYLENEDIAMINE

V. V. Korshak, Z. M. Frunze and V. V. Kurashev, Vysokomol. soedin. **2**: No. 5, 633–635, 1960.

PHOSPHORUS-containing polyamides have been obtained by the interface polycondensation of oxy-bis(*p*-carboxyphenyl)phenylphosphinyl dichloride and hexamethylenediamine. The viscosity of the polyamides has been investigated as function of the reactant concentration. The method used permits polymers of higher molecular weight to be obtained than in the case of polycondensation in the melt.

ADHESION OF HIGH POLYMERS—VI. THE EFFECT OF THE MOLECULAR WEIGHT OF BUTADIENEACRYLONITRILE COPOLYMERS OF VARIOUS POLARITIES ON THEIR ADHESION TO POLAR AND NON-POLAR SUBSTRATES

V. L. Vakula, Khe Iun-csui, V. E. Gul' and S. S. Voiutskii, Vysokomol. soedin. **2**: No. 5, 636–645, 1960.

THE EFFECT of the molecular weight of butadieneacrylonitrile copolymers of various polarities on their adhesion to a polar (polyamide) and non-polar (polyisobutylene) substrate at room and elevated contact temperatures has been investigated. The adhesion of each of the copolymers investigated has been shown to fall with increase in molecular weight up to a certain limit (300,000–350,000), above which its value remains practically constant. Increase in the contact temperature raises the adhesion of all fractions. The adhesion of butadieneacrylonitrile copolymers of constant molecular weight at room contact temperatures is little dependent upon the polarity of the adhesives. Heating of the bond increases its strength in different degrees, depending upon the polarity of the copolymers. The adhesion of unfractionated rubbers to polyamide at room contact temperature is determined by the polydispersity of the product, whereas at elevated temperatures the acrylonitrile content of the polymer is the decisive factor.

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The adhesion of butadieneacrylonitrile copolymers to a non-polar substrate has been shown to be independent of their polarity, molecular weight and temperature of contact. The results of the investigation have been interpreted in terms of the diffusion theory of adhesion.

SYNTHESIS OF POLYDIMETHYLSILOXYALKYLENEFUMARATES AND THEIR COPOLYMERIZATION WITH STYRENE

M. A. Bulatov and S. S. Spasskii, Vysokomol. soedin. **2**: No. 5, 658–661, 1960.

THE alcoholysis of dimethyldiethoxysilane by low molecular polyesters of fumaric acid yielded silicon-containing polyesters capable of copolymerization with vinyl monomers to form insoluble solids.

A study of the copolymerization of these polyesters with styrene showed that incorporation of organosiloxane units in the polyesters chain has no significant effet on the character of the copolymerization.

STUDIES OF COORDINATION POLYMERS—IV. SYNTHESIS OF POLYMERS ON THE BASIS OF AROMATIC BIS-(β-DIKETONES) WITH METALS

V. V. Korshak, E. S. Krongaus and V. E. Sheina, Vysokomol. soedin. **2**: No. 5, 662–672, 1960.

A DESCRIPTION has been presented of the synthesis of some aromatic bis-(β-diketones),isophthalyldiacetophenone, 4,4′-bis(acetoacetyl)-diphenyloxide, 4,4′-bis(acetoacetyl)diphenyl and β, β, β′, β′-tetra-acetyldiethylbenzene. The compounds have been used as the basis for the formation of polymers with Be, Cu, Ni, Co, Zn, Cd, Mn.

A discussion has been made of the relation between the properties of the polymers and the structure of the original bis-(β-diketones).

HETEROCHAIN POLYAMIDES—XXIV. FORMATION OF MIXED POLYAMIDES AT THE INTERFACIAL BOUNDARY

V. V. Korshak, T. M. Frunze, L. V. Kozlov and A. Yu. Alybina, Vysokomol. soedin. **2**: No. 5, 673–678, 1960.

IT has been shown that mixed polyamides may be synthesized by non-equilibrium polycondensation at the interfacial boundary during interaction between adipyl, azetyl, sebacyl, terephthalyl and isophthalyl chlorides with hexamethylenediamine. The difference in reactivities of adipyl, isophthalyl and terephthalyl chlorides has been found to exert no effect on the composition of the resultant mixed polyamide.

MERCURATION OF RUBBER—II. MERCURATION OF BUTADIENE RUBBERS WITH *p*-NITROBENZOYL CHLORIDE

R. N. Smirnov, Vysokomol. soedin. **2**: No. 5, 679–684, 1960.

THE conversions of four mercurated butadiene rubbers of varying mercury content taking place during reaction with p-$NO_2C_6H_4COCl$ have been investigated. The difference in the structure and probably in the nature of the chemical bond between mercury atoms and polybutadienes as compared with mercurated olefines is especially brought to the fore in the reactions with p-$NO_2C_6H_4COCl$ in alkaline medium, during which the following conversions take place: substitution of mercury, esterification of the hydroxyl group, cyclization and vulcanization by oxygen, oxido-reduction of the macromolecules and halogenation. Evidently such a complexity of reactions is associated with the involved structure of the mercurated rubbers in question.

PHOSPHORUS-CONTAINING POLYMERS—II. THE APPLICATION OF THE ARBUZOV REARRANGEMENT FOR THE SYNTHESIS OF POLYPHOSPHONATES

K. A. Petrov, E. E. Nefantev and I. I. Sopikova, Vysokomol. soedin. **2**: No. 5, 685–688, 1960.

HERETOFORE unknown cyclic phosphinites have been obtained by the reaction of dichlorophosphines with glycols. The reaction leads to the desired result if phenyldichlorophosphine is employed as the dichlorophosphine and 1,3-glycol as the glycol. The resulting compounds polymerize on heating with a small quantity of methyl iodide in a sealed tube. (For 1 mole phosphite 0·001–0·1 mole methyl iodide is employed.) The compounds formed are polyphosphonates of molecular weight 270–3200. The structure of the polymers has been demonstrated by their decomposition with phosphorus pentachloride yielding phenyl-(1-methyl-3-chloropropyl)-phosphinyl chloride. The above procedure is a novel method for synthesizing phosphorus-containing polymers.

SYNTHESIS OF HIGH MOLECULAR AROMATIC POLYAMIDES BY INTERFACIAL POLYCONDENSATION IN ACID MEDIA

L. B. Sokolov and T. V. Kudim, Vysokomol. soedin. **2**: No. 5, 698–703, 1960.

THE interfacial polycondensation of aromatic diamines with aromatic dicarboxylic acid chlorides has been investigated over a wide range of pH values of the aqueous phase. It has been shown that polyamides of the highest molecular weights are formed in the acid region.

SOME RELATIONSHIPS IN INTERFACIAL POLYCONDENSATION

L. B. Sokolov and T. L. Kruglova, Vysokomol. soedin. **2**: No. 5, 704–709, 1960.

A study has been made of the joint interfacial polycondensation of diamines and dicarboxylic acid chlorides. It has been shown that the dependence upon the initial mixture composition may be satisfactorily expressed by the equation $[A]/[A_0]=([B]/[B_0])^a$.

Remarks have been made upon the reaction sites of interfacial polycondensation.

THE EFFECT OF THE SOLVENT CAPACITY OF THE ORGANIC PHASE IN THE INTERFACIAL SYNTHESIS OF POLYAMIDES

L. B. Sokolov and L. V. Turetskii, Vysokomol. soedin. **2**: No. 5, 710–715, 1960.

A STUDY has been made of the effect of the solvent capacity of the organic phase on the molecular weight of polyamides in inferfacial polycondensation. The molecular weights have been shown to have maximum values at definite (optimal) values for this capacity. The effect of temperature and ultrasonic waves on the molecular weights of polyamides in relation to the properties of the solvent used as organic phase has been investigated.

SYNTHESIS AND POLYMERIZATION OF MIXED 8-MEMBERED ORGANOSILOXANES

K. A. Andrianov, L. M. Khananashvili and Yu. F. Konopchenko, Vysokomol. soedin. **2**: No. 5, 719–727, 1960.

THE joint hydrolysis of dimethyldichlorosilane and methylvinyldychlorosilane yielded the new compounds: heptamethylvinylcyclotetrasiloxane, hexamethyldivinylcyclotetrasiloxane, pentamethyltrivinylcyclotetrasiloxane. By the joint hydrolysis of dimethyldichlorosilane

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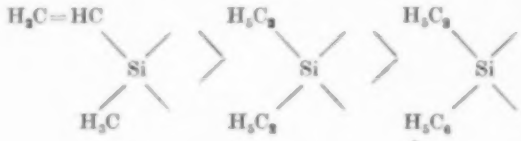
and diethyldichlorosilane, hexamethyldiethylcyclotetrasiloxane was obtained. The joint hydrolysis of dimethyldichlorosilane and ethylphenyldiethoxysilane produced hexamethylethylphenylcyclotetrasiloxane.

The catalytic polymerization of the organosiloxanes was investigated and it was found that in line with the intensity of the effect upon the degree of polymerization the organosiloxane groups in the 8-membered ring arrange themselves in the following series.



FILLED POLYMERS—II. THE EFFECT OF DISPERSING AMINATED BENTONITE IN THE MONOMER UPON THE REINFORCEMENT OF POLYMETHYLMETHACRYLATE

I. A. Uskov and T. A. Kusnitsyna, Vysokomol. soedin. **2**: No. 5, 728–730, 1960.

HIGHLY disperse octadecylaminated bentonite was incorporated in polymethylmethacrylate by fine dispersion in the monomer medium containing the polymerization initiator (benzoylperoxide). The ultimate dispersion of the filler to primary particles carried out in the monomer medium and the uniform distribution of the former over the entire body of the polymer led to considerable increase in its hardness in the glass state and to improvement of its thermostability. Dispersion to such a state is effected by means of a vibro-mill. The resultant material is 47% harder than polymethylmethacrylate and its flow temperature is raised by not less than 60°.

THE SWELLING OF CARBOXYL RESINS IN WATER–METHANOL MIXTURES

Lou Chzi-syan, E. M. Savitskaya and B. P. Bruns, Vysokomol. soedin. **2**: No. 5, 745–750, 1960..

THE kinetics of swelling and compression of dried and moist carboxyl resins of the Li- and H-forms in aqueous and methanol solutions have been investigated. Preliminarily dried Li-forms of cation exchangers have been found to swell very slowly in methanol. The equilibrium specific volumes of the salt and hydrogen forms of the cation exchangers in water-methanol mixtures of varying concentrations have been determined. It has been found that above a certain methanol content in the mixture the specific volume of the salt form of the resin is less than that of the hydrogen form. The specific volumes of the resins charged with bivalent ions are for all concentrations of methanol in the solution less than the specific volumes of resins with univalent counter ions.

INORGANIC ION EXCHANGE ON CARBOXYL CATION EXCHANGERS IN WATER–METHANOL MIXTURES

Lou Chzi-syan, E. M. Savitskaya and B. P. Bruns, Vysokomol. soedin. **2**: No. 5, 751–758, 1960.

THE course if inorganic ion exchange on monofunctional carboxyl resins in varying water-methanol mixtures has been investigated.

The rate of exchange diminishes with increasing methanol content in the mixture. In the case of the salt forms of the resin the fall in rate is connected with a decrease in the specific volumes of the exchangers in that form with increasing methanol content. The fall in rate in the case of the hydrogen forms under the same conditions is probably due

to the decrease in value of the dissociation constant of the carboxyl exchanger. The equilibrium value of relative acidity of the medium expressed through pH_p in which the same degree of substitution of the H-ions of the resin by metallic ions is attained increases with the methanol concentration.

THE SYNTHESIS OF RESINS ON THE BASIS OF 3- AND 4-NITROPHTHALIC ACIDS AND POLYATOMIC ALCOHOLS AND INVESTIGATION OF SOME CORRELATIONS IN THEIR POLYCONDENSATION

E. V. Kuznetsov, A. P. Bogdanov and A. P. Gill, Vysokomol. soedin. **2**: No. 5, 759–764, 1960.

IT has been found that under the same conditions 4-nitrophthalic acid, its anhydride and chloride engage more easily in polycondensation reactions that the corresponding 3-nitrophthalic compounds. The resins of the 4-compounds with polyatomic alcohols possess higher molecular weights than the corresponding 3-compounds.

Under equal conditions of condensation, depending upon the nature of the acid component the molecular weights of the resins have been found to increase in the order: acid→anhydride→acid chloride; the acid numbers of the resins diminish in the order; anhydride→acid→acid chloride.

Twelve alkyd resins have been synthesized on the basis of the nitrophthalic acids and polyatomic alcohols, 8 resins being obtained for the first time.

STUDIES ON POLYCARBONATES—I. THE EFFECT OF THE MOLECULAR WEIGHT ON THE TRANSITION TEMPERATURES OF POLYCARBONATES

P. V. Kozlov, L. Makaruk, V. N. Fomin and V. I. Olkhovskii, Vysokomol. soedin. **2**: No. 5, 770–777, 1960.

AN investigation was made into the effect of the molecular weight on the thermomechanical properties and transition temperatures of poly-2,2-bis-(4′-hydroxphenyl) propane carbonates. The fractionated polycarbonates with wide ranges of molecular weights (from 5000 to 220,000) have been shown to assume an intermediate position between crystalline and amorphous polymers. Polycarbonates of low mean molecular weights are by their thermomechanical characteristics typical crystallizing compounds; the high molecular products possess the characteristic features of amorphous rigid chain polymers. The mechanical segment of the polycarbonates has been determined. It attains a value of about 40 units. Assuming a position between polyisobutylene and polyvinylchloride, i.e., possessing a sufficiently large chain flexibility the polycarbonates are at the same time rigid polymers of high strength. Such an anomaly is explained by the specific three-dimensional structure of the molecules, strong molecular interaction and, apparently, by the specific features of their secondary structural formations.

THERMOMECHANICAL STUDIES OF AMORPHOUS AND CRYSTALLINE POLYMERS

A. V. Sidorovich and E. V. Kuvshinskii, Vysokomol. soedin. 2: No. 5, 778–784, 1960.

A THERMOMECHANICAL study has been made of the softening of crystalline polymers during uniform, uniaxial stretch and also of the effect of the rate of heating upon the softening of amorphous polymers. The effect of the tensile force on the thermomechanical behaviour

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of various polymers has been followed over the range 20 to 100kg/cm² and within wide temperature limits (–150° to 250°). Ribbons 50mm long, 2–4mm wide and 0·05 to 0·5mm thick served as specimens.

Of the crystalline polymers the study included: isotactic polypropylene, polyethylene, polytetrafluoroethylene and polyethyleneterephthalate; of the amorphous: polyethyleneterephthalate and styrene-butadiene SKS-80 copolymer.

The simplest thermomechanical curves were those of the amorphous linear isotropic polymers. The curves are characterized by a point of inflexion—abrupt increase in deformation on reaching the softening point. The thermomechanical curves of crystalline polymers are more complicated and are characterized by three differing regions of creep: below the glass temperature, cold flow and the beginning of melting.

SYNTHESIS OF NEW CELLULOSE AND OTHER POLYSACCHARIDE DERIVATIVES—IX. THE SYNTHESIS OF THE ESTERS OF CELLULOSE WTH AMINO ACIDS

Sun Tun, V. A. Derevitskaya and Z. A. Rogovin, Vysokomol. soedin. **2**: No.5, 785–790, 1960.

CELLULOSE esters with various amino acids (β-alanin, ε-aminocaproic acid and ζ-aminoenanthic acid) have been synthesized by interaction of cellulose with the hydrochlorides of the amino acid chlorides. A relation has been established between the structure of the amino acids and their capacity for acylating cellulose.

SYNTHESIS OF CHELATE POLYMERS

N. A. Glukhov, M. M. Koton and Yu. V. Mitin, Vysokomol. soedin. **2**: No. 5, 791–792, 1960.

CHELATE polymers from tetraketones and divalent metals have been obtained by interfacial condensation at 40–60°. The melting point of the polymers depends mainly upon the nature of the metallic constituent of the chain, decreasing with increasing atomic number of the metal.

POLYANHYDRIDES FROM PHTHALIC AND MIXED PHTHALIC AND ADIPIC ACIDS

K. A. Andrianov, G. P. Bochkareva, A. G. Prelkova and N. N. Sokolov, Vysokomol. soedin. **2**: No. 5, 792–796, 1960.

THE polyanhydrides of terephthalic and of isophthalic acids have been synthesized, and their thermomechanical and dielectric properties have been investigated. The mixed polyanhydrides of terephthalic and adipic and of isophthalic and adipic acids have been prepared for the first time. A study has been made of their chemical and thermomechanical properties.

A DILATOMETRIC STUDY OF THE POLYMERIZATION KINETICS OF *p*-HALOGEN SUBSTITUTED (IN THE RING) STYRENES

O. V. Kallistov, Vysokomol. soedin. **2**: No. 5, 797–801, 1960.

A KINETIC study has been made of the polymerization of *p*-substituted (in the ring) styrene halides. From kinetic data on the beginning stages of the polymerization process the activation energies have been determined for *p*-fluorostyrene, *p*-chlorostyrene, *p*-bromostyrene, *p*-iodostyrene and the unsubstituted styrene.

A description has been given of the dilatometric method used for the kinetic studies.

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THE EFFECT OF THE CHEMICAL STRUCTURE OF SOME UNSATURATED ESTERS UPON THEIR POLYMERIZATION CAPACITY

A. I. Volkova, M. M. Koton and M. N. Savitskaya, Vysokomol. soedin. **2**: No. 5, 802–805, 1960.

It has been found that the esters of acrylic acid polymerize more rapidly than their isomeric vinylesters. The incorporation of a chlorine atom into the alkyl group of the unsaturated ester as well as lengthening of the radical slows down the polymerization process.

SOME PRE-TRANSITIONAL PHENOMENA IN THE VICINITY OF THE CRITICAL MIXING TEMPERATURE OF THE SYSTEM POLYMER–SOLVENT

V. E. Eskin and S. Ya. Margarik, Vysokomol. soedin. **2**: No. 5, 806–807, 1960.

A sharp increase in the flow birefringence of polystyrene solutions ($M = 2{\cdot}4 \times 10^5$) in cyclohexane has been revealed in the vicinity of the critical mixing temperature. This alongside other effects goes to make up the general complex of pre-transitional phenomena in the system polymer—solvent.

THE SHAPE OF ETHYLCELLULOSE MOLECULES

V. N. Tsvetkov and I. N. Shtennikova, Vysokomol. soedin. **2**: No. 5, 808–816, 1960.

Flow birefringence of ethylcellulose in tetrachlormethane, bromoform and ethyl acetate has been studied over the range of molecular weights 3×10^4 to 1×10^5. The internal (segmental) anisotropy of the macromolecules was determined. It has been found to be of positive sign and independent of the molecular weight.

Considerable shape birefringence was revealed, proportional to the molecular weight of the polymer and to the square increment of the refractive index.

A quantitative comparison of the experimental data with conclusions following from the existent theory show that the hydrodynamic and optical properties of ethylcellulose do not correspond to Gaussian coils but may be satisfactorily described by means of the equivalent ellipsoid model, the shape asymmetry of which exceeds by several fold ($p = 23$) that of the "normal" Gaussian coil.

EFFECT ON POLYDISPERSITY ON THE LIGHT SCATTERING OF POLYMER SOLUTIONS—II

Yu. Ya. Kolbovskii, Vysokomol. soedin. **2**: No. 6, 825–827, 1960.

The angular distribution of scattered light has been calculated for polydisperse Gaussian coils in the case of the Schultz molecular weight distribution. The light scattering method has been shown to be applicable for determining the type of molecular weight distribution and the distribution parameter.

THE EFFECT OF POLYDISPERSITY ON THE END-TO-END DISTRIBUTION FUNCTION OF FREE-ROTATING CHAINS

Yu. Ya. Kolbovskii, Vysokomol. soedin. **2**: No. 6, 828–831, 1960.

Distribution functions have been obtained for the absolute values of the end-to-end distances of free-rotating chains in the case of polydisperse system. Non-fractionated polymers have been considered as the polydisperse systems (Bresler-Frenkel, Schultz and Lansing–Cramer distributions).

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SOME FACTORS AFFECTING THE ADHESION OF RUBBERS TO CORD IMPREGNATED WITH LATEX-PROTEIN COMPOSITIONS

A. A. Berlin, R. V. Uzina and I. L. Shmurak, Vysokomol. soedin. **2**: No. 6, 832–837, 1960.

THE effect of pH of a latex-protein adhesion strengthening composition on the strength of the cord to rubber bond has been investigated. It has been suggested that the behaviour of the proteins in the latex-protein impregnations is associated with the amino acid composition of the proteins. The degree of asymmetry of casein and keratein molecules has been determined and curves have been obtained, depicting the dependence of time of flow of their solutions through a capillary upon the pressure at various pH values. The fall in strength of the bond between the latex-protein impregnated cord and rubber with increase in pH has been shown to be connected with increase in rigidity and change in shape of the ionized protein molecules.

ON HETEROCHAIN POLYAMIDES—XXV. SYNTHESIS AT THE INTERFACIAL BOUNDARY OF POLYAMIDES CONTAINING PIPERAZINE UNITS

V. V. Korshak, T. M. Frunze and L. V. Kozlov, Vysokomol. soedin. **2**: No.6, 838–844, 1960.

A DESCRIPTION has been presented of polyamides synthesized by the interfacial polycondensation of piperazine with adipyl, azelyl, sebacyl, phthalyl, isophthalyl and terephthalyl chlorides and of ethylenehexamethylene and non-amethylene-diamine with sebacyl chloride. Binary systems have been obtained of mixed polyamides of sebacyl chloride with mixtures of piperazine and ethylene-, hexamethylene- and non-amethylenediamine in varying proportions. It has been found that the flow temperatures and the solubilities of the polyamides on the basis of piperazine and the chlorides of aliphatic dicarboxylic acids depend upon the number of methylene groups in the acid and also upon whether they are of odd or even number. For the polyamides obtained from aromatic dicarboxylic acids and piperazine the flow temperatures and solubilities depend upon the position (*o*-, *m*-, *p*-) of the carboxyl groups in the ring.

The incorporation of 20 mole% aliphatic diamine residues in polypiperazine-sebacamide brings about a fall in its flow temperature. Further increase in aliphatic diamine content, however, leads to an increase in the flow temperature and a decrease in solubility of the mixed polyamides. It has been found that the difference in reactivity of piperazine and hexamethylenediamine under the given conditions does not affect the composition and properties of the mixed polyamide.

ON HETEROCHAIN POLYAMIDES—XXVI. MIXED POLYAMIDES OF PIPERAZINE WITH ALIPHATIC AND AROMATIC DICARBOXYLIC ACIDS

V. V. Korshak, T. M. Frunze and L. V. Kozlov, Vysokomol. soedin. **2**: No. 6, 845–850, 1960.

A DESCRIPTION has been given of mixed polyamides obtained by the interfacial polycondensation of piperazine with adipyl, azelyl, phthalyl, isophthalyl and terephthalyl chlorides. The incorporation of aliphatic dicarboxylic acid units into the polyamides has been shown to markedly decrease the flow temperature of the polymer. The relative positions of the carboxyls in the aromatic dicarboxylic units of the mixed polyamides obtained on the basis of piperazine exert the usual effects; the highest melting products being the polyamides containing the *p*-phenylene ring. Polyamides synthesized from piperazine are characterized

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by higher solubilities in the conventional organic solvents than those obtained from other aliphatic diamines. Mixed polyamides obtained from piperazine and azelyl, phthalyl and isophthalyl chlorides dissolve better than all others in polar organic solvents.

CONCENTRATION DEPENDENCE OF THE DIFFUSION COEFFICIENT OF ORGANIC SUBSTANCES IN POLYMERS

R. M. Vasenin, Vysokomol. soedin. **2**: No. 6, 851–856, 1960.

An equation has been proposed, describing the change in the intrinsic coefficient of diffusion with the concentration of the diffusing substance:

$$D = D_{\varphi_1=0}\left(\frac{D_{\varphi_1=1}}{D_{\varphi_1=0}}\right)^{1-e^{\beta\varphi_1/(1-\varphi_1)}}$$

The equation holds for all ranges of concentration from the pure polymer to the pure solvent.

The derivation of the equation is based on the following assumptions: (a) The rate of diffusion is proportional to the probability of formation of a microcabity; (b) The probability of formation of a microcavity depends upon the amount of energy required for its formation; (c) The energy of formation of a microcavity is a function of the composition of the system.

COEFFICIENT OF DIFFUSION AND THE NATURE OF THE DIFFUSING MOLECULES

R. M. Vasenin, Vysokomol. soedin. **2**: No. 6, 857–863, 1960.

In the diffusion of paraffins or olefines in polymers of this or that chemical nature the resistance to the molecular motion may be associated with the presence of two retarding effects: namely "viscous" and "frontal" resistances. Viscous resistance is determined by the mometum transmitted in unit time by the molecule to the macromolecules of the medium. It depends upon the quantity of kinetic units (groups) of the molecule and hence upon its mass. The presence of double bonds decreases the amount of kinetic units, leading to a fall in viscous resistance. The frontal resistance is determined by the cross-section of the molecule. The diffusion coefficient of the substance may be calculated from the formula

$$D = \frac{D_1}{\sigma^{\alpha} n}\left(\frac{2n-q}{2n-2q}\right)$$

where D_1 is the diffusion coefficient of methane, n the number of carbon atoms, q the number of double bonds in the molecule, σ the relative molecular cross-section, α a constant, characteristic of the diffusion medium.

THE SORPTION OF DYES BY SYNTHETIC CARBOXYLATED ION EXCHANGERS

G. Ya. Gerasimov, L. F. Yakhontova, and B. P. Bruns, Vysokomol. soedin. **2**: No. 6, 864–870, 1960.

Ion exchange taking place on carboxyl exchanges with the participation of large ions of basic type dyes has been investigated. The sorption of the dyes methylene blue, antipyrene red and of the previously investigated basic antibiotics has the same specific features. The common behaviour in the sorption process points out to a common distribution of the ions in the resin after exchange.

In the study of the sorption of antibiotics the picture of ion distribution in the resin was made only on the basis of the kinetics and statics of the ion exchange reaction.

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The study of dyes sorption gave a means of visual observation of ion distribution under any conditions of exchange. The ion distribution as revealed visually completely confirmed the earlier concepts of the process based on the study of the relationships holding in the sorption of large organic ions.

COMPARISON OF POLYMER CHARACTERISTICS MEASURED WITH THE AID OF DIFFERENT INSTRUMENTS

G. L. Slonimskii and V. A. Ershova, Vysokomol. soedin. **2**: No. 6, 871–874, 1960.

An illustrative analysis of the operation of two types of dynamometers clearly showed the influence of the rigidity of their construction and the influence of the properties of the specimen undergoing measurement on the establishment of strain conditions during stretching at constant rate of motion of the clamp. The different strain conditions caused by this factor may lead to differences in the dependence between the conditional stress and the strain, owing to relaxation phenomena.

SYNTHESIS AND INVESTIGATION OF UNSATURATED POLYAMIDES

O. Ya. Fedotova and S. P. Brysina, Vysokomol. soedin. **2**: No. 6, 875–878, 1960.

The possibility of synthesis has been demonstrated of the heretofore undescribed linear and tridimensional polyamides from maleic anhydride (I) and the symmetric diaminodiarylmethanes: 4,4′-diamino-3,3′-dimethyldiphenylmethane (II) and its *N*,*N*′-diethyl derivative (III).

The activation energy of the reaction of II and I is ~14,000–15,000 kcal/mole, the extent of the polycondensation ~16, the molecular weight ~5000.

The activation energy of the reaction of III and I is ~20,000 kcal/mole, the extent of polycondensation ~30, the molecular weight ~9000.

Under the influence of air and light, on heating the melt and as a film in the cold, the polymers are capable of passing over into the non-melting and insoluble state. In the absence of light and air they retain their double bond and hence their solubility for 3–4 weeks.

COPOLYMERIZATION OF POLYETHYLENEGLYCOLFUMARATEPHOSPHINATE WITH THE ALLYL DERIVATIVES OF PHOSPHORUS ACIDS

M. E. Mat'kova and S. S. Spasskii, Vysokomol. soedin. **2**: No. 6, 879–883, 1960.

A study has been made of the copolymerization of polyethyleneglycolfumaratephenylphosphinate with the allyl derivatives of the acids of phosphorus. The monomer reactivities have been determined for the systems polyethyleneglycolfumaratephosphinateallyl diethylphosphinoacetate: $r_1 = 1{\cdot}73 \pm 0{\cdot}03$; $r_2 = 0{\cdot}15 \pm 0{\cdot}06$ and for polyethyleneglycolfumaratephosphinate with diethylallylphosphinic acid: $r_1 = 2{\cdot}07 \pm 1{\cdot}12$; $r_2 = 0{\cdot}09 \pm 0{\cdot}95$.

On the basis of the values obtained for the monomer reactivities it has been shown that the allyl derivatives of phosphorus acids are more reactive towards that polyester radical in copolymerization with phosphorus-containing polyfumarates than with polyfumarates.

SYNTHESIS AND INVESTIGATION OF HIGH MOLECULAR TERTIARY AMINES BASED ON QUATERNARY AMMONIUM COMPOUNDS FROM COPOLYMERS OF 2-METHYL-5-VINYLPYRIDINE AND VARIOUS "CROSS-LINKING" AGENTS

A. B. Davankov and L. B. Zubakova, Vysokomol. soedin. **2**: No. 6, 884–890, 1960.

High molecular quaternary ammonium bases have been synthesized by alkylating granulated copolymers of 2-methyl-5-vinylpyridine with divinylbenzene and ditriethyleneglycol and methacrylate and the properties of the bases have been investigated.

SYNTHESIS AND INVESTIGATION OF AROMATIC POLYAMIDES

O. Ya. Fedotowa, I. P. Losev, Yu. P. Brysin and N. F. Pugachevskaya, Vysokomol. soedin. **2**: No. 6, 899–903, 1960.

It has been shown that highly thermostabile polyamides may be synthesized by condensation of aromatic diamines with dimethyl terephthalate. The kinetics of the reaction between dimethyl terephthalate and benzidine, toluidine, 4,4′-diaminodiphenylmethane and 4,4′-diamino-3,3′-dimethyldiphenylmethane have been investigated, the optimal conditions for the synthesis of the thermostabile polyamides being established. The properties of the polymers and methods of their treatment have been described. The nature of the plasticizing action of the methylene bridge between the aromatic rings as well as of the substituent in the diamine nucleus on the properties of the aromatic polyamides has been revealed.

INVESTIGATION OF STRUCTURAL CHANGES IN FIBRES BY MEASUREMENTS OF THEIR SPECIFIC SURFACE AREAS AND THEIR PORE VOLUMES

V. A. Berestnev, T. V. Gatovskaya and V. A. Kargin, Vysokomol. soedin. **2**: No. 6, 916–925, 1960.

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Adsorption isotherms have been obtained of η-hexane on viscose fibres subjected to various treatments, of iso-octane on capron cord and on the maximum disintegrated (by mastication) cord and of water on all these materials. Calculations based on the sorption data allowed the changes in structure undergone by the fibres as the result of various treatments to be evaluated. On the basis of the findings a general picture has been presented of the possible changes in the structure of a fibre, leading to its disintegration.

FILLED POLYMERS – III. POLYMERIZATION OF METHYLMETHACRYLATE DURING THE DISPERSION OF SODIUM BENTONITE

I. A. Uskov, Vysokomol. soedin. **2**: No. 6, 926–930, 1960.

In the vibro-disintegration of air-dry sodium bentonite blocks in methylmethacrylate medium, polymerization of the monomer takes place and the grafting of the polymethylmethacrylate to the disperse bentonite particles, to the amount of 22% of the filler. The homopolymer practically does not form in this process. In the presence of benzoyl peroxide concurrently with the formation of the graft polymer polymerization takes place in the homogeneous phase. The optimal quantities of bentonite increase the rate of polymerization of methylmethacrylate in the presence of benzoyl peroxide scores of times. Excess bentonite leads to practically complete inhibition of the polymerization.

STUDIES ON POLYCARBONATES—II. ELECTRON MICROSCOPIC INVESTIGATION ON THE STRUCTURE OF POLYCARBONATES

L. Makaruk, P. V. Kozlov and V. A. Kargin, Vysokomol. soedin. **2**: No. 6, 931–936, 1960.

An electron microscopic study has been described of the secondary structures of poly 2,2′-bis-(4′-hydroxyphenyl)-propane carbonates arising:(a) as the result of vaporization of the solvent; (b) on precipitation of the polycarbonate from solution by lowering the temperature; on adding a non-solvent to the solution.

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In the first two cases a fibrillar structure is formed with a very high asymmetry of the fibriles. These owe their appearance to association of the primary structures—packets of chains—and do not change their morphological picture whether the chains in the packets are in the crystalline or amorphous states. From these studies there follows an interpretation of the specific mechanical properties of the polycarbonates, especially their high impact strength.

THERMODYNAMIC INVESTIGATION OF THE INTERACTION OF GRAFT COPOLYMERS WITH THE SOLVENT

M. M. Iovleva, P. V. Kozlov and V. A. Kargin, Vysokomol. soedin. **2**: No. 6, 937–941, 1960.

THE integral heats of swelling of graft copolymers of polystyrene and polyacrylic acid in benzene have been determined. Isotherms of benzene sorption by the graft copolymer with a polyacrylic acid content of 29 molar per cent have been obtained and the values of $\Delta\bar{z}_1$ and $\Delta\bar{s}_1$ have been calculated.

On the example of the above system it has been shown that in the swelling of diphilic types of graft copolymers a decisive part is played by the energy effect. The entropy effect remaining negative as in the initial polystyrene does not facilitate the swelling process.

ELUCIDATION OF THE RELATION BETWEEN STRUCTURE AND ORIENTATION OF MOLECULAR CHAINS OF POLYETHYLENETEREPHTHALATE

N. V. Mikhailov, O. A. Klueva, V. O. Gorbacheva and E. Z. Fainberg, Vysokomol. soedin. **2**: No. 6, 942–946, 1960.

THE effect of the drawing temperature on the elastic properties and structure of films and fibres of polyethyleneterephthalate has been examined.

It has been shown that in the process of heating the stretched fibres and films, alongside a decrease in the degree of crystallinity desorientation of the secondary structural formations may be observed.

CARBOCHAIN POLYMERS AND COPOLYMERS – XXIV. SYNTHESIS OF GRAFT COPOLYMERS BY THE INTERACTION OF POLYMETHYMETHACRYLATE AND POLYPENTAMETHYLENETHIODIVALERATE

H. S. Kolesnikov and Tsen Khan-min, Vysokomol. soedin. **2**: No. 6, 947–951, 1960.

GRAFT copolymers of polymethylmethacrylate with polypentamethylenethiodivalerate of various composition have been obtained by interaction of the two polymers and the effect of the composition on the properties of the copolymers has been investigated. That the products are graft copolymers has been shown by turbidimetric titration. The interaction between polymethylmethacrylate and polypentamethyllenethiodivaleate has been shown to take place at a very high rate.

NEW METHOD OF SYNTHESIS OF GRAFT COPOLYMERS

V. V. Korshak, K. K. Mozgova and M. A. Shkolina, Vysokomol. soedin. **2**: No. 6, 957–958, 1960.

THE proposed new method of synthesis of graft copolymers consists in heating specimens of polyamide or polyester films or fibres for some time in air or nitrogen and then subjecting them to copolymerization in block with vinyl monomers. The resultant copolymers possess higher mechanical strength than the initial compounds.

X-RAY INVESTIGATION OF THE INFLUENCE OF TEMPERATURE ON THE STRUCTURE OF POLYAMIDE FIBRES

A. V. Ustinova and N. S. Andreeva, Vysokomol. soedin. **2**: No. 6, 958–959, 1960.

In the course of X-ray diffraction studies of two polyamides (capron and enant) at low temperatures change in the X-ray pattern with the temperature was observed. Instead of one strong meridional reflection corresponding to the projection of one bond on the fibre axis two strong meridional reflections appeared. This points to structural transformations of the polyamides with decrease in temperature. The investigations are continuing.

HETEROCYCLIC POLYESTERS—XXVII. A STUDY OF SOME CORRELATIONS POLYESTERIFICATION TAKING PLACE AT THE INTERFACIAL BOUNDARY

V. V. Korshak, S. V. Vinogradova, A. S. Lebedeva, Vysokomol. soedin. **2**: No. 7 977–983, 1960.

A study has been made of the effect of the initial reagent ratio, sodium hydroxide content and monofunctional additions on the reduced viscosity and yield of the polyester of isophthalic acid and *p*, *p'*-dihydroxydiphenylpropane obtained by interfacial polycondensation.

It was found that when the reaction is carried out at 1:2 dihydroxydiphenylpropane-sodium hydroxide molar ratios maximum molecular weight polyester is obtained for equimolar ratios of isophthalyl chloride to dihydroxyldiphenylpropane. Maximum molecular weight polyester (provided dihydroxydiphenylpropane and isophthalyl chloride are taken in equimolar quantities) is obtained when sodium hydroxide is 1.1–1·2 times the equimolar content of dihydroxydiphenylpropane. Addition of monofunctional substances of the type of acyl chlorides or phenol to the mixture lowers the yield and molecular weight of the polyester.

ON HETEROCHAIN POLYAMIDES—XXVII. THE SYNTHESIS OF MIXED POLYAMIDES FROM HOMOPOLYAMIDES

V. V. Korshak, T. M. Frunze and Lu I-nan', Vysokomol. Soedin. **2**: No. 7, 984—988, 1960.

A study has been made of the formation of mixed polyamides on heating various mixtures of two homogeneous polyamides and it has been shown that the conversion of homopolymer mixtures to copolymers proceeds through the intermediate stage of block copolymers. A scheme has been proposed for the change in composition of the system in the course of the reaction.

POROSITY OF ION-EXCHANGE RESINS

A. A. Tager, Vysokomol. Soedin. **2**: No. 7, 994—996, 1960.

A theoretical discussion has been made of the microporosity of sorbents. It has been suggested that the concept of "porosity" or "microporosity" is applicable only to solid, rigid sorbents, It may not be applied to elastic polymers or swelled cross-linked resins since these are devoid of permanent voids, i. e. pores not changing with time.

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POROSITY OF ION-EXCHANGE RESINS—II

A. A. Tager, A. B. Pashkov, M. V. Tsilipotkina and N. I. Bykova, Vysokomol. soedin. **2**: No. 7, 997—1000, 1960.

THE vapour adsorption isotherms of carbon tetrachloride (inert liquid) and methyl alcohol (active liquid) have been obtained on the ion-exchange resins KU-2. The resins are sulphur-containing products of copolymerization of styrene and divinylbenzene, the amount of the latter being from 2 to 16%. The over-all pore volumes were calculated from the CCl_4 adsorption isotherm with the aid of the Dubinin-Radushkevich equation, the values found being by an order of magnitude less than those for polystyrene and two orders less than those for finely porous activated carbon. It thus follows that the unswelled ion exchanger possesses insignificant microporosity. The cause of the high sorption capacity of the resins is not their porosity but the considerable swelling power, as follows from the data on methyl alcohol sorption.

THE OPTICAL ANISOTROPY AND THE SHAPE OF SILOXANE POLYMER MOLECULES IN SOLUTION

V. N. Tsvetkov, E. V. Frisman and N. N. Boitsova, Vysokomol. soedin. **2**: No. 7, 1001—1009, 1960.

THE flow birefringence of polydimethylsiloxane (PDMS) and polydimethylphenylsiloxane (PDMPS)solutions has been investigated. The molecular coil asymmetry has been determined. This has been found to be somewhat lower than the values usually obtained for Gaussian chains in solution.

The segment anisotropy has been determined and the anisotropy of the monomeric unit of PDMS and PDMPS as well as the anisotropy difference of the SiC and SiO groups have been calculated.

CARBOCHAIN POLYMERS AND COPOLYMERS—XXV. THE ACTION OF UNSATURATED ACID CHLORIDES ON POLYVINYLALCOHOL

Tsen Khan-min and H. S. Kolesnikov, Vysokomol. soedin. **2**: No. 7, 1010—1012, 1960.

BY the interaction of polyvinylalcohol with unsaturated acid chlorides products are formed the properties of which differ from those of the initial polyvinylalcohol. Treatment of polyvinylalcohol films with vinylphosphinyl chloride makes them inflammable; films treated with methacrylyl chloride possess greater tensile strength and less extensibility than the initial products.

QUANTITATIVE DETERMINATION OF RESIDUAL MONOMER IN POLYSTYRENE WITH THE AID OF THE ULTRAVIOLET ABSORPTION SPECTRA

V. N. Mironova and V. V. Zharkov, Vysokomol. soedin. **2**: No. 7, 1013—1014, 1960.

A METHOD has been developed for the quantitative determination of styrene in foamed polystyrene and in styrene-methylmethacrylate copolymers by means of the ultraviolet absorption spectra with a relative error of $\pm 1{\cdot}5\%$. By use of the "base lines" method the accuracy of determination of the styrene does not diminish in the presence of a number of addition agents despite their absorption in the ultraviolet region.

SPECTROSCOPIC MANIFESTATIONS OF HYDROGEN BONDING IN POLYAMIDES

V. N. Nikitin and B. Z. Volchek, Vysokomol. soedin. **2**: No. 7, 1015—1019, 1960.

THE changes in intensity of the 3080 and 3280 cm^{-1} bands in a polyamide with respect to the temperature, conditions of film casting, quenching and deuteration of the oriented specimens have been determined by means of an infrared spectrometer with a LiF prism. The band intensities of the oriented specimens were measured in polarized infrared light. The optical density of the 3280 cm^{-1} band has been shown to diminish on melting of the crystallites. Quenching also lowers the optical density of the band. The intensity of the band is affected by the temperature of film casting. Deuteration of the oriented specimens leads to an increase in dichroism of the 3280 cm^{-1} band, which is associated with substitution of the hydrogen by deuterium in the amorphous, less oriented part of the polymer. The data obtained show that the 3280 cm^{-1} band is characteristic of the hydrogen bond in the crystalline and amorphous parts of the polymer. Its intensity is determined by the ratio of these parts.

Similar investigations with the 3080 cm^{-1} band show that it is characteristic mainly of the hydrogen bond in the amorphous part of the polymer.

SOME PROPERTIES OF AROMATIC AND ARYLALIPHATIC POLYAMIDES PREPARED BY INTERFACIAL POLYCONDENSATION—I

O. Ya. Fedotova, M. L. Kerber and L. P. Losev, Vysokomol. soedin. **2**: No. 7, 1020—1025, 1960.

BY means of the interfacial polycondensation method polyamides were obtained in the series of aromatic diamines and sebacyl and terephthalyl chlorides, among them the heretofore undescribed: poly-3,3′-dimethyldiphenylsebacamide, polydiphenylethaneterephthalamide, poly-*m*-tolyleneterephthalamide, polydiphenylmethaneterephal-*N*, *N*′-dimethylamide, polydiphenylmethaneterephthal-*N*, *N*′-dimethylamide, poly-*p*-phenyleneterephthalamide and poly-3,3′-dimethyldiphenylmethaneterephthal-*N*, *N*′-diethylamide.

A comparison of the melting points of the polymers with those of the corresponding polyamides obtained by means of equilibrium polycondensation showed the former to be higher than the latter.

The effect has been shown of the state of the diamine (base, salt) on the yield and melting point of the polymer. When the diamine is reacted in the form of a salt the yield of the polymer is higher, but the melting point lower.

It has been found that in the case of non-equilibrium polycondensation higher yields are obtained for polymers from aromatic than from aliphatic diamines.

INVESTIGATION OF THE FINE MOLECULAR STRUCTURE OF ORIENTED REGENERATED CELLULOSE FIBRES

N. V. Mikhailov, E. Z. Fainberg and M. Kozler, Vysokomol. soedin. **2**: No. 7, 1031—1038, 1960.

THE fine molecular structure of three types of oriented regenerated cellulose fibres has been investigated by measuring the density of the latter in the dry and moist states and by determining the partial heats of wetting.

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The results obtained in the study of the relation between the true fiber density and the water content may be used in passing judgement on the structural homogeneity of the fibres. It has been shown that improved physico-mechanical characteristics of cord fibres are brought about by uniform distribution of the intermolecular bonds with respect to number and energies.

DISMYMMETRY OF THE CRITICAL OPALESCENCE OF POLYSTYRENE IN CYCLOHEXANE SOLUTION

V. E. Eskin, Vysokomol. soedin. **2**: No. 7, 1049—1055, 1960.

MEASUREMENTS of the dismymmetry of the critical opalescence carried out in cyclohexane solutions of very narrow polystyrene fractions make it possible to calculate the dimensions of low molecular polystyrene coils. The dimensions were in qualitative agreement with those determined from the molecular weight and intrinsic viscosity of the fractions. There is greater deviation when M is lowered from 2×10^5 to 2×10^4.

The shape of the dismymmetry curves indicates that further light must be thrown on this phenomenon.

A STUDY OF THE FLOW BIREFRINGENCE OF ISOTACTIC POLYSTYRENE FILMS

O. V. Kallistov and E. V. Korneeva, Vysokomol. soedin. **2**: No. 7, 1056—1061, 1960.

THE flow birefringence of isotactic polystyrene films has been investigated. The flow birefrigence and photoelastic coefficient have been found to depend upon the time of heating the films above the softening temperature. It was noted that such a relationship is associated with the initial phase of crystallization of the film.

A correlation has been obtained between the photoelastic coefficient and temperature for the isotactic polymer. The method employed in the study of the photoelastic properties of isotactic polystyrene films has been described.

THE ROLE OF THE HYDROGEN BOND IN THE LINKING OF IONS TO PROTEINS

E. A. Bauman, Vysokomol. soedin. **2**: No. 7, 1063—1066, 1960.

THE linking of the complex anions ferritrioxalates and chromitrioxalates to native and iodinated proteins has been investigated. The degree of binding has been shown to be related to the number of basic groups in the protein molecule.

The concept regarding the mechanism of linkage of complex anions developed by the author is in disagreement with that of Clotz in which the degree of binding of the anions is considered to be affected by the mutual screening of the protein groups by hydrogen bombs.

MECHANISM OF THE THERMAL HARDENING OF PHENOL-FORMALDEHYDE RESINS

Z. S. Smirnova and V. L. Serenkov, Vysokomol. soedin. **2**: No. 7, 1067—1070, 1960.

THE thermal hardening of resols is due to interaction between methyl groups and the hydrogen of the ring. The hydroxyl groups of phenol do not participate chemically in the hardening process. The phenol hydroxyls undergo no change when novolaks are heated to 180° and even to 250°C. Heating the latter to 350°C leads to their degradation.

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INVESTIGATION OF THE POLYALUMOETHYLSILOXANE CATALYZED POLYMERIZATION OF POLYORGANOSILOXANES

K. A. Andrianov and A. A. Zdhanov, Vysokomol. soedin. **2**: No. 7, 1071—1076, 1960.

IT has been established that in the polymerization of polyorganosiloxanes under the influence of polyalumoethylsiloxanes co-ordination bonds are formed between aluminum atoms of the polyalumoethylsiloxane chain and oxygen atoms of the polyorganosiloxane.

POLYMERIZATION OF DIVINYLACETALS

L. A. Arbuzova and K. Sultanov, Vysokomol. soedin. **2**: No. 7, 1077—1081, 1960.

THE polymerization of divinylacetals has been investigated. The divinyl compounds were obtained by removal of hydrogen chloride from bis(2-chloroethyl) acetals prepared by interaction of ethylene chlorohydrin with aldehydes in the presence of calcium chloride.

The conditions were established for bulk polymerization in the presence of radical initiators, leading to the synthesis of linear polymers, in general of a cyclic structure. New linear polymers, of divinylethylal and divinylbutyral have been obtained. These are amorphous powders, soluble in organic solvents.

Polymerization on solution induced by ionic catalysts led to the formation of insoluble tri-dimensional polymers.

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EFFECT OF FILLERS ON THE MELTING POINTS OF CRYSTALLINE POLYMERS

V. A. Kargin and T. L. Sogolova, Vysokomol. soedin. **2**: No. 7, 1093—1098, 1960.

A STUDY has been made of the melting points and mechanical properties of crystalline polymers compounded with solid fillers. The addition of a filler not entering into chemical reaction with the polymer has been shown not to shift its melting point, i. e. it does not break down the structure of the primary crystalline regions. It does, however, change the complex of mechanical properties, i. e., it affects the secondary crystalline formations. On chemical interaction between the filler and the polymer the melting point of the latter is lowered. The filling of a crystalline polymer with large amounts of metallic oxides causes a qualitative change in the properties of the polymer at temperatures above the melting point.

SYNTHESIS OF CYCLIC ORGANOSILICON COMPOUNDS WITH PHENYLENESILOXANE CHAINS IN THE MOLECULE

K. A. Andrianov and V. E. Nikitenkov, Vysokomol. soedin. **2**: No. 7, 1099—1102, 1960.

THE hydrolysis in acid medium has been investigated of 1,4-bis(methyldichlorosilane)-benzene and 1-methyldihlorosilane-4-phenyldichlorosilane-benzene. The reaction has been shown to lead to polymers with phenylenesiloxane chains in the molecule, prone to structuration at moderate temperatures.

The mechanism of hydrolysis and of condensation has been studied and it has been shown that the formation of polymers with phenylenesiloxane chains proceeds via the formation of cyclic compounds possessing high reactivities.

The mechanism of formation of the polymers has been established on the bases of the new cyclic crystalline compounds isolated.

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STUDIES OF THE SPHERULITE STRUCTURE IN POLYMERS—IV. X-RAY STUDY OF MACROSPHERULITES OF POLYETHYLENESEBACATE

N. G. Esipova, Li Pan-tun, N. S. Andreeva and P. V. Kozlov, Vysokomol. soedin. **2**: No. 7, 1109—1118, 1960.

An X-ray study has been made of the macrospherulites of polyethylenesebacate. The unit cell dimensions and the orientation of the cell with respect to the spheruliteradius have been determined from the X-ray diagrams obtained for a single radial element, the macrospherulite fibrile. It has been shown that the direction of the *a* axis of the unit cells coincides with that of the spherulite radius; the molecular chains are arranged with respect to the fibrillar axis at an angle equal to the monoclinal angle of the cell (about 65°).

The thickness of the cell packet in the direction of the spherulite radius has been calculated from low angle scattering data.

THE SYNTHESIS OF UNSATURATED POLYAMIDES AND POLYESTERS BY INTERFACIAL POLYCONDENSATION

H. S. Kolesnikov and A. S. Maloshitskii, Vysokomol. soedin. **2**: No. 7, 1119—1121, 1960.

Unsaturated polyamides and polyesters were synthesized by the interfacial polycondensation of fumaryl chloride and various diamines and diphenols. The polyamides were shown to possess an ordered structure.

DIFFUSION OF DEXTRAN FRACTIONS IN WATER

L. F. Shalaeva, Vysokomol. soedin. **2**: No. 8, 1137—1143, 1960.

The values for the coefficients of translational diffusion, intrinsic viscosities and molecular weights of dextran fractions have been obtained over a wide range of molecular weights (40×10^3–234×10^6). On the basis of the data obtained a relation has been found between the diffusion coefficient and molecular weight which for the high molecular fraction has an exponent of 0·34. The constant $A = \frac{(\Phi')^{1/3}}{P^{\sigma}} k$ has been calculated for the low molecular fraction. Its value is close to that for linear polymers.

ON THE CONFORMATION OF THE STRETCHED POLYMER CHAIN

Yu. Ya. Kolbovskii, Vysokomol. soedin. **2**: No. 8, 1144—1147, 1960.

A distribution function for a stretched chain of non-restricted linkage without calculation of the statistical chain integral has been derived on the basis of the general solution for the random wandering problem.

OPTICAL ANISOTROPY OF THE MACROMOLECULES OF POLYSTYRENE DERIVATIVES

E. V. Frisman, A. M. Martsinovskii and N. A. Domnicheva, Vysokomol. soedin. **2**: No. 8, 1148—1153, 1960.

The segmental optical anisotropy of some polystyrene derivatives has been determined from flow birefringence measurements. The rotation of the side chains of polyparachloro-

styrene, poly-2,5-dimethylstyrene and polystyrene has been shown to be of identical character. In order to explain the observed segmental anisotropy of poly-2,5-dichlorostyrene one must assume the rotation of its side chains to differ from those of polystyrene.

EFFECT OF POLYDISPERSITY ON THE LIGHT SCATTERING OF POLYMER SOLUTIONS – III

Yu. Ya. Kolbovskii, Vysokomol. soedin. **2**: No. 8, 1154—1156, 1960.

THE effect of polydispersity on light scattering by solutions of rigid polymer molecular rods has been examined. The light scattering indicatrix for various molecular weight distributions has been calculated.

HETEROCHAIN POLYESTERS—XXVIII. INVESTIGATION OF SOME CORRELATIONS IN INTERFACIAL POLYESTERIFICATION

V. V. Korshak, S. V. Vinogradova, A. S. Lebedeva, Vysokomol. soedin. **2**: No. 8, 1162—1166, 1960.

A STUDY has been made of the effect of various emulsifiers and of the catalytic action of various substances on the intrinsic viscosity and yield of the polyester of dian and isophthalic acid, obtained by interfacial polycondensation.

It has been shown that polyesters of the highest molecular weight (intrinsic viscosity in cresol 1·44 and 1·54) are formed with nekal and with the sodium salts of fatty sulphoacids (merzolyat) as emulsifiers. The use of an emulsifier widens the number of organic solvents applicable in interfacial polycondensation to form the polyester of dian and isophthalic acid.

POLYMERIZATION OF CYCLOHEXADIENE

P. A. Shantarovich and I. A. Shlyapnikova, Vysokomol. soedin. **2**: No. 8, 1171—1175, 1960.

THE termal polymerization of cyclohexadiene has been investigated. It has been shown that below 200°C the main product is the dimer. Dimerization of cyclopentadiene obeys second order reactions kinetics. Evidently the reaction takes place with the formation of a biradical of the type of diallyl which as a result of self-saturation transforms to the final product (dimer). The activation energy of the dimerization reaction is 22kcal/mole.

MODIFICATION OF POLYVINYLCHLORIDE BY RUBBERS

A. A. Berlin, A. G. Kronman, D. M. Yanovskii and V. A. Kargin, Vysokomol. soedin. **2**: No. 8, 1188—1192, 1960.

A STUDY has been made of the polymerization of vinylchloride in the presence of various rubbers and also of the joint plasticization of polyvinyl chloride with rubbers at elevated temperatures. The polymerization of vinylchloride in the presence of butadiene-nitrile rubber was accompanied by the formation of graft copolymers. The physicomechanical properties of vinylplasts prepared on the basis of products obtained in the modification of polyvinylchloride by various rubbers do not exceed the corresponding properties of ordinary vinylplast. Vinyplastics prepared from the coplasticization products of polyvinylchloride with polar group containing rubbers (nairite and butadiene-nitrile rubbers) have superior strength properties to vinyplast from polyvinyl-chloride, probably due to hydrogen bondage between polyvinylchloride and rubber molecules.

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MECHANOCHEMICAL MODIFICATION OF SKS-30

N. K. Baramboim and B. V. Sautin, Vysokomol. soedin. **2**: No. 8, 1196—1200, 1960.

THE mechanochemical bonding of maleic anhydride by SKS-30 and polyisobutylene during mastication has been investigated. It has been shown that the binding is due to the free macroradicals of the polymer formed in the mechanocracking process.

INTERACTION OF SULPHUR AND NATURAL RUBBER BY THE ACTION OF IONIZING RADIATION

Z. N. Tarasova, M. Ya. Kaplunov, V. T. Kozlov, N. A. Klauzen and B. A. Dogadkin, Vysokomol. soedin. **2**: No. 8, 1201—1206, 1960.

THE effect of sulphur on the kinetics of the radiation structuration of natural rubber and the properties of the radiation vulcanizates have been investigated. At 25°C a marked addition of sulphur under the action of the radiation is observed, the amount increasing with increasing dose in conformity with a curvilinear relationship. The rate of addition increases with the temperature. The presence of sulphur diminishes the effect of structuration. Increase in temperature during the irradiation from −80 to 100° causes an intensification in the structuration. With pure rubber at temperatures above 50° reversion of the structuration process takes place; in the presence of sulphur this phenomenon is not observed. On irradiating natural rubber and its mixtures with sulphur in argon a significant fall in unsaturation is observed, the fall being less marked in the presence of sulphur.

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POLYMERIZATION OF SUBSTITUTED N-PHENYLMETHACRYLAMIDES—II

G. M. Chetyrkina, T. A. Sokolova and M. M. Koton, Vysokomol. soedin. **2**: No. 8, 1207—1212, 1960.

FIVE new compounds, namely, *p*-carbamino-, *p*-methylcarbamino-, *p*-cyanophenylmethacrylamide and *o*- and *p*-carboethoxyphenyl methacrylate have been synthesized and described. The polymerization of a number of *N*-phenylmethacrylamides in dimethyl-formamide has been investigated and it has been shown that incorporation of electrophilic substituents into phenyl residues accelerates the polymerization reaction in comparison with non-substituted phenylmethacrylamide. Polymerization in bulk of the phenylmethacrylates showed them to polymerize slower than the analogous amides of metacrylic acid. In the series of phenylmethacrylates the para-isomer polymerizes faster than the ortho-isomer, whereas in the case of *N*-phenylmethacrylamides the presence of intermolecular hydrogen bonds in the para-isomers retards the polymerization rate of these compounds. On incorporating the polar groups $-CN$, $-CONH_2$ and $-CONHCH_3$ in the phenyl residue of methacrylamide the resultant polymers possess higher softening temperatures, but are brittle. Polymers of substituted *N*-phenylmethacrylamides possess higher glass temperatures than the corresponding polyphenylmethacrylates.

INVESTIGATION OF THE VULCANIZATION OF POLYCHLOROPRENE LATEXES—I. VULCANIZATION BY MEANS OF HYDROLYSIS

D. M. Sandomirskii and E. M. Spector, Vysokomol. soedin. **2**: No. 8, 1221—1226, 1960.

THE ageing of polychloroprene latexes of the type of nairite L-4 at room and elevated temperatures has been investigated. A study was made of the effect of hydrolysis, as the

basic factor in the ageing of polychloroprene in latex, on the physicomechanical properties of films obtained by drying of nairite latexes. The hydrolysis of polychloroprene increases the tensile strength of the films, without changing the relative elongation values. The addition of alkali greatly accelerates the process. The heating of the latex in the presence of alkali may be regarded as a sort of "vulcanization" of the polymer in the latex.

STUDIES IN GRAFT COPOLYMERIZATION—VI. FRACTIONATION OF GRAFT COPOLYMERIZATION PRODUCTS OF VINYL CHLORIDE WITH BUTYL METHACRYLATE—METHACRYLIC ACID COPOLYMER

A. A. Berlin, L. V. Stupen', V. I. Fedoseev and D. M. Yanovskii, Vysokomol. soedin, **2**: No. 8, 1227—1233, 1960.

THE possibility of separating graft copolymerization products of vinyl chloride with the butyl methacrylate—methacrylic acid copolymer (BMK-5) by fractional precipitation or extraction has been investigated. The solubilities of polyvinylchloride and BMK-5 were found to be mutually affected when present together both in solution or in a coprecipitated mechanical mixture. This is explained by the formation of molecular associates of the homopolymers. The formation of associates does not permit isolation of homopolymer-free graft copolymer from the polymerization products nor separation of the coprecipitated mixture of homopolymers, despite the large difference in solubilities of polyvinylchloride and BMK-5.

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STRUCTURE OF THE MOLECULAR CHAIN OF POLYETHYLENE PRODUCED WITH THE AID OF γ-RAYS

I. G. Soboleva†, N. V. Makletsova and S. S. Medvedev, Vysokomol. soedin. **2**: No. 8, 1234—1238, 1960. † *Deceased*

POLYETHEYLENE produced in the gaseous phase by gamma-ray initiated polymerization at 25°C with doses not exceeding 4×10^6 roentgens and intensities up to 82 roentegns/sec is characterized by a low degree of molecular chain branching. For equal radiation intensities, ethylene concentrations and polymerization temperatures the mean molecular weight increases with radiations dose. For equal doses the molecular weight increases with falling intensity. When at the same doses, intensities and ethylene concentrations the temperature is raised to 50° an increase in the molecular weight of polyethylene and in the degree of branching of its molecular chain is observed.

THE ROLE OF OXYGEN IN THE POLYMERIZATION OF VINYLIDENE CHLORIDE

G. A. Razuvaev and K. S. Minsker, Vysokomol. soedin. **2**: No. 8, 1239—1245, 1960.

THE part played by oxygen in the polymerization of vinylidene chloride has been investigated. It has been shown that during the induction period the monomer reacts with oxygen to form a solid crystalline peroxide, easily determined iodometrically. The peroxide was isolated and some of its properties were investigated. The composition of the peroxide was determined from the mean result of analyses of its specimens and on the basis of its decomposition products. In all probability it is not an individual substance, approaching

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in composition the formula $[xC_2H_3Cl_2yO_2 - \text{loss of HCl}]$. The average values of x and y are most often 3 and 2 respectively. The accumulation of the peroxide in the induction period has been studied during polymerization in an atmosphere of air in a closed vessel with and without initiator—azoisobutyrodinitriel (ADN). Despite the continuous decrease in oxygen concentration of the gaseous phase, the peroxide was found to increase linearly with time. The activation energy of the over-all process was calculated from the temperature dependence. In the case of non-initiated oxidation of the monomer $E = 9{\cdot}8$ kcal/mole, wheras in the presence of ADN $E = 38{\cdot}5$ kcal/mole. The presence of molecular oxygen in the reaction zone during polymerization of vinylidene chloride leads to the appearance of by-groups ($C=C,C-O-$, $-O-O-$) bearing a negative influence on the quality of polyvinylidenechloride.

COPOLYMERIZATION OF DICHLOROSTYRENES AND CHLOROMETHYLSTYRENES WITH STYRENE

A. F. Dokukina, Z. A. Smirnova and M. M. Koton, Vysokomol. soedin. **2**: No. 8, 1247—1254, 1960.

THE copolymerization of a number of chloro-and chloromethyl substituted styrenes with styrene in bulk at $t = 60°C$ has been investigated. The relative monomer reactivity constants have been determined and the relative reactivities of the substituted styrenes for the styrene radical as well as the activity factors Q and e have been calculated. It has been shown that in respect of the decreasing reactivity the monomers form a series analogous to that obtained by us in studies on homopolymerization.

SYNTHESIS AND INVESTIGATION OF POLYAMIDOUREA

O. Ya. Fedotova and Mao Bin-tsoan, Vysokomol. soedin. **2**: No. 8, 1255—1260, 1960.

POLYMERS not described heretofore have been obtained from poly-3,3'-dimethyldiphenylmethanesebac-N,N'-diethyl/dibutyl amides and hexamethylenediisocyanate (EG, RPG, BG) as well as tolylene diisocyanate (ET, PT, BT). The reaction of the polyamides with diisocyanates has been found to take place both at the imino and at the carboxyl end groups with the formation of polyamidoureas, the molecular weight of the polymer increasing by 4–5 fold in comparison with that of the starting materials. The reaction of diisocyanate with the polyamide takes place in the melt and in solution, the yield being higher in the first case at moderate temperatures, the values of which depend upon the structure of the polyamide. Determination of the strain–temperature relation showed that the new polymers have flow temperatures in the region of 150–200° (EG, PG, BG) and 220–250° (ET, PT, BT) and also clearly defined high elastic regions, absent in the initial polyamides.

INTERACTION OF bis-(CHLOROMETHYL) TETRAMETHYLDISILOXANE WITH HEXAMETHYLENEDIAMINE

K. A. Andrianov and L. M. Volkova, Vysokomol. soedin. **2**: No. 8, 1261—1265, 1960.

THE polycondensation of bis-(chloromethyl)tetramethyldisiloxane and bis-(chloromethylemthylphenyl) disiloxane with hexamethylenediamine has been investigated. The reaction begins on slight heating and proceeds with a large heat effect. The products are cyclic compounds. Three new cyclic compounds have been isolated.

CARBOCHAIN POLYMERS AND COPOLYMERS—XXVI. POLYMERIZATION AND COPOLYMERIZATION OF 1,1,2-TRICHLOROBUTADIENE-1,3

H. S. Kolesnikov, A. P. Suprun and T. A. Soboleva, Vysokomol. soedin. **2**: No. 8, 1266—1269, 1960.

It has been shown that 1,1,2-trichlorobutadiene-1,3 polymerizes according to a radical mechanism and a study has been made of the effect of the molecular weight of the polymer on its thermomechanical properties. Copolymers of 1,1,2-trichlorobutadiene-1,3 with methylmethacrylate and with styrene have been obtained of various composition and their thermomechanical properties have been determined. 1,1,2-Trichlorobutadiene-1,3 has been found to copolymerize also with acrylonitrile, vinyl chloride, vinyl acetate, isoprene and bicyclo-(2,2,1)-heptadiene-2,5.

STUDIES OF MOLECULAR INTERFRACTION IN POLYMERS—I. THE APPLICATION OF INFRARED SPECTROSCOPY TO STUDIES OF AVETYLCELLULOSE

R. G. Zhbankov, R. V. Zueva, L. V. Savel'eva and P. V. Kozlov. Vysokomol. soedin. **2**: No. 8, 1270—1279, 1960.

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The specific features of the chemical structure of the entire series of polymer-analogues of cellulose acetate from the triacetate to the almost completely saponified product have been investigated by the aid of infrared spectroscopy. It has been found that at the beginning of the saponification process restoration takes place chiefly of the primary hydroxyl groups and the kinetics of restoration of the various regions of the hydroxyl band contour over the entire course of the reaction may yield certain information on the properties of the product. With respect to the OH frequencies the cellulose acetates have been shown to assume a position intermediate between nitrocellulose and cellulose. The increase in viscosity of dilute acetate solutions in *m*-cresol on liberation of the bound acetic acid has been explained by association of the macromolecules due to intermolecular hydrogen bonding. It has been suggested that the primary hydroxyl groups possess weaker hydrogen bonds from an energy standpoint than the secondary. The insolubility of the product at a certain stage of saponification in *m*-cresol has been found to be accompanied by an abrupt increase in the absorption in the region of the probably position of the frequencies of hydroxyls participating in intermolecular hydrogen bonds of the type OH. . . . .OH. . . . . OH. The fundamental bands in the spectra of the products in the region 3600–400 cm^{-1} have been interpreted.

INVESTIGATION OF THE STRUCTURE OF POLYAMIDES OBTAINED BY THE INTERFACIAL POLYCONDENSATION METHOD

N. V. Mikhailov, V. O. Gorbacheva, V. P. Kovaleva and O. A. Klyueva, Vysokomol. soedin. **2**: No. 8, 1283—1286, 1960.

A tentative study has been made of the structures and properties of the polyamides 66 and 610, prepared by the interfacial condensation method, with respect to their molecular weights and polydispersities. It has been shown that the polyamides obtained by interfacial polycondensation are of identical structure as those from the melt and differ only in the kinetics of structuration. It has been shown that with decrease in molecular weight of the polyamide fractions degeneration of the fibrillar structure of the polymer takes place.

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COPOLYMERIZATION OF BORON-SUBSTITUTED BORAZOLS WITH HEXAMETHYLENEDIISOCYANATE

V. V. Korshak, V. A. Zamyatina, N. I. Bekasova and Ma Zhui-zhan, Vysokomol. soedin. **2**: No. 8, 1287, 1960.

BY reaction of boron-substituted borazols with hexamethylenediisocyanate polymers are formed containing borazol in the chain.

EFFECT OF INGREDIENTS ON THE FROST RESISTANCE OF RUBBER DURING REPEATED DEFORMATION

V. D. Zaitseva and G. M. Bartenev, Vysokomol. soedin. **2**: No. 9, 1301—1308, 1960.

A STUDY has been made of the effect of various low molecular plasticizers on the frost stability of SKN 40, SKS 30, and MV-pyridine rubbers during repeated deformation (within the frequency range 0·1–1000 oscillations/min). It has been shown that the plasticizers exert a greater effect on polar than on non-polar rubbers due to different mechanisms of action on the two types of rubbers. The difference between polar and non-polar rubbers is also manifested in differences between the actions of the plasticizers at high and low deformation frequencies on the intermolecular structure and frost resistance of the rubbers. The incorporation of carbon black and chalk has been shown to leave practically unchanged the frost resistance of the rubbers, but to widen the glass transition region in the direction of higher temperatures. The simultaneous incorporation in the rubber stock of plasticizer and carbon black lowers the frost resistance of the rubber and the more so, the greater the black content. Hardness (dynamic modulus) significantly increases with incorporation of filler, which is an additional factor in lowering the frost resistance of rubbers.

COPOLYMERIZATION OF UNSATURATED POLYESTERS WITH VINYL MONOMERS—X. THERMOMECHANICAL INVESTIGATION OF COPOLYMERS OF THREE COMPONENT SYSTEMS

S. S. Spasskii and T. V. Molchanova, Vysokomol. soedin. **2**: No. 9, 1320—1323, 1960.

A THERMOMECHANICAL study has been carried out of the copolymerization of three component systems comprising an unsaturated polyester and two vinyl monomers. The reactivity ratios for the unsaturated polyesters and vinyl monomers have been shown to reflect the course of the copolymerization and to be applicable to calculations of the copolymer compositions. The monomer reactivity constants for the low molecular mono-and diesters of fumaric acid and vinyl monomers cannot be employed in calculating the composition of unsaturated polyester copolymers.

MECHANICAL AND DIELECTRIC LOSSES OF POLYVINYLETHYAL IN THE GLASS STATE

S. P. Kabin, Vysokomol. soedin. **2**: No. 9, 1324—1329, 1960.

THE results are described of investigations on the rate and attenuation coefficients of longitudinal and shear waves in polyvinylethylal at 1 mc/s frequencies and temperatures ranging from 20 to 80°C. The velocity of the shear waves was varied from $1{\cdot}2 \times 10^5$ cm/sec to $1{\cdot}1 \times 10^5$ cm/sec and the amplitude attenuation coefficient from $a = 1{\cdot}03$ 1/cm to $a_2 = 1{\cdot}46$ 1/cm.The longitudinal wave velocity varied from $v_1 = 2{\cdot}08 \times 10^5$ cm/sec to $1{\cdot}96 \times 10^5$

cm/sec. A maximum amplitude attenuation coefficient of $\alpha = 0{\cdot}45$ 1/cm was observed at 50°C. On the basis of α and v measurements the shear, longitudinal compression, and volumetric compression moduli and the Poisson coefficient μ, as well as the corresponding slopes of the mechanical losses, have been calculated. It has been shown that in the aforementioned temperature range mechanical relaxation losses appear on volumetric deformation of polyvinylethylal. Maximum mechanical losses are observed at the same temperature as maximum dielectric losses. $\mu = 0{\cdot}25$ at 25°C and 0·28 at 80°C.

INVESTIGATION INTO THE SYNTHESIS AND APPLICATION OF HIGH MOLECULAR COMPOUNDS CONTAINING THIOL AND THIONE GROUPS

A. B. Davankov and E. V. Zambrovskaya, Vysokomol. soedin. **2**: No. 9, 1330—1334, 1960.

In order to prepare sulphydryl containing styrene-divinylbenzene copolymers two paths of synthesis were selected; namely, (1) treatment of the chloromethylated copolymer with a thiourea solution and subsequent hydrolysis and (2) diazotation of the aminated copolymer followed by xanthogenation and hydrolysis.

By means of the first method the sulphur content of the product (SDT cation exchanger) varied from 11 to 15%, depending upon the conditions of reaction. The yield was 70–80% of the weight of the added copolymer. The sorptive capacity of the SDT exchanger varied very little with pH of the solution.

With the aid of the second method the cation exchanger SNK containing 5·1 to 6·1% sulphur was obtained.

The dynamic exchange capacity determined with respect to the cation Ag^+ from a 0·1 N $AgNO_3$ solution was 2·7–2·8 meq/g for SDT and 2·13 meq/g for SNK. The sorption of silver ions was alternated with their reduction on the resin to the metal by means of a 10% hydrosulphate or sodium sulphate solution in order to regenerate the functional groups of the exchanger and concentrate silver in large amounts. On the exchanger SDT 238.7% silver with respect to the resin or 22·1 meq/g with respect to the metal was concentrate in the course of 8 sorption reduction cycles.

INVESTIGATION OF DIFFUSION PROCESSES IN SOME POLYMERS—III. IRREVERSIBLE CHANGE IN DIFFUSION CHARACTERISTICS BY ACTION OF ^{60}Co GAMMA IRRADIATION OF THE POLYMER

N. S. Tikhomirova, Yu. M. Malinskii and V. L. Karpov, Vysokomol. soedin. **2**: No. 9, 1335—1349, 1960.

The diffusion of helium and argon through polymers subjected to various integral doses of gamma radiation has been investigated.

The diffusion rate of helium and argon in SKS–30, polyethylene and polyamides diminishes with increasing integral dose, which is evidently due to formation of cross inks. In contrast to these polymers gaseous diffusion through polytetrafluoroethylene increases with the absorbed dose (> 2·0 Mrad.). For a dose of 250 Mrad, the permeability of polyvinylchloride also increases ~ fourfold.

The solubility constants for argon decrease with increase in dosage for polyethelene and polyamide and increase for polytetrafluoroethylene.

The activation energy of diffusion and the enthalpy and entropy of dissolution of the gases in the polymer rise in the case of polyamides and fall for polyethylene, depending upon the over-all dose.

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A linear relation exists between the pre-exponential factor of the temperature dependence of diffusion D_0 and the activation energy of diffusion of gases in the irradiated polymers.

The variations in D_0 equal two orders of magnitude, depending upon the dose, hence D_0 is the most sensitive indicator of structural changes in polymers subjected to irradiation.

No after-effects have been observed in polyethylene, polyamides or polytetrafluoroethylene. After-effects may be explained by the existence for several days of free radicals that gradually undergo interaction.

INVESTIGATION OF DIFFUSION PROCESSES IN SOME POLYMERS—IV. REVERSIBLE CHANGES IN DIFFUSION CHARACTERISTICS DURING RADIATION

N. S. Tikhomirova, Yu. M. Malinskii and V. L. Karpov, Vysokomol. soedin. **2**: No. 9, 1349—1359, 1960.

STUDY has been made of the diffusion of the monoatomic gases helium and xenon through polyethylene and polytetrafluoroethylene during irradiation by ^{60}Co.

A reversible effect of the radiation on the diffusion rate of gases in polymers has been established; namely, during irradiation the gaseous permeability of the polymers sharply increases, after the radiation source has been removed the permeability assumes its former value.

The reversible effect in gas diffusion is observed both for structurizing polymers (polyethylene) as well as destructurizing ones (polytetrafluoroethylene). The large rise in the diffusion rate cannot be explained by the temperature rise of the film during irradiation, the latter in the authors' experiments being responsible for not more than 1/6 of the measured effect.

The rise in the diffusion rate during irradiation differs for different polymers. Thus the permeability of polyethylene increases 10–15 fold, whereas for polytetrafluoroethylene the increase is twofold (on intensive irradiation at 700 r/sec). The reversible radiodiffusion effect depends linearly upon the dose energy within the limits investigated.

Special experiments have shown that the increase in permeability of the polymers during irradiation is associated with the increase in the rate of gas diffusion in the polymer but not with increase in solubility of the gas in the polymer.

The acceleration of gaseous diffusion in polyethylene during irradiation is greater for gases with large atomic diameters.

POLYCONDENSATION OF HALOALKY(HALOARYL)HALOSILANES BY THE ACTION OF METALLIC SODIUM

V. V. Korshak, A. M. Polyakova, A. A. Sakharova, V. F. Mironov and E. A. Chernyshev, Vysokomol. soedin. **2**: No. 9, 1370—1374, 1960.

THE polycondensation of haloalky(haloaryl)halosilanes of the varying structure, induced by metallic sodium has been investigated. The polymers were isolated, their properties determined and their structure established.

THE USE OF WURTZ REACTION FOR THE SYNTHESIS OF POLYSYLYLENE POLYMERS—I. REACTION BETWEEN METALLIC SODIUM AND DICHLOROMETHYL DERIVATIVES OF AROMATIC HYDROCARBONS

E. P. Melnikova, A. A. Vansheidt, M. G. Krakovyak and L. V. Kukhareva, Vysokomol. soedin. **2**: No. 9, 1383—1390, 1960.

IT has been found that the Wurtz reaction in dioxane solution at 20–25° may be used to synthesize poly-*p*-xylylenes of the general structure $(CH_2\text{–}Ar\text{–}CH_2)_n$ starting from *bis*-chloromethyl derivatives of a number of aromatic hydrocarbons. Polydimethylene-*m*-xylene

containing CH_2 groups in the meta position was distinguished by ready solubility in chloroform and low molecular weight varying from 1800 to 4000 depending upon the conditions of synthesis. Polydimethylene derivatives of benzene, *p*-xylene and diphenylmethane with CH_2 groups in the para position dissolved only in high boiling solvents, forming low viscosity solutions. Polydimethylenediphenyl and polydimethylenenaphthalene were insoluble in organic solvents, including high boiling ones being apparently crosslinked (three-dimensional) polymers.

X-RAY STUDY OF ORIENTED GUTTA-PENCIL FILMS IN THE REGION OF THE MELTING TEMPERATURES

V. I. Selikhova, G. S. Markova and V. A. Kargin, Vysokomol. soedin. **2**: No. 9, 1398—1401, 1960.

It has been shown that the melting of oriented gutta-percha films is accompanied by gradual transition of the gutta-percha from the α to β and further to the γ modification. The temperature regions of existence and the differences in orientation of all three modifications have been established. The melting of oriented gutta-percha films irradiated with γ-rays from a ^{60}Co source (radiation dose 75×10^6–100×10^6 r.) has been found to proceed differently than with nonirradiated specimens.

POLYMERIZATION OF DIVINYLBENZAL

I. A. Arbuzova, R. R. Kostikov and L. N. Propp, Vysokomol. soedin. **2**: No. 9, 1402—1404, 1960.

Divinylbenzal has been synthesized by removal of hydrogen chloride from di-(β-chloroethyl) benzal. The latter was obtained by heating ethylene chlorohydrine with benzaldehyde in the presence of a catalyst (hydrochloric acid) and solvent (benzene).

On radical induced polymerization of divinylbenzal linear polymers were obtained, soluble in benzene, chloroform, dioxane and pyridine and containing from 3 to 5% of residual unsaturation.

The properties of the polymers indicated that polymerization proceeded according to a cyclic mechanism with the formation of six-membered dioxane rings.

POLYVINYLAMINE AND ITS DERIVATIVES—I. SYNTHESIS OF POLYVINYLAMINE AND ITS CARBOXYMETHYL DERIVATIVE FROM POLYVINYLSUCCINIMIDE

S. S. Skorokhodov and A. A. Vansheidt, Vysokomol. soedin. **2**: No. 9, 1405—1408, 1960.

Polyvinylamine has been obtained by the alkaline hydrolysis of low molecular weight polyvinylsuccinimide on heating to 80–90° under ordinary pressure. The carboxymethylation of polyvinylamine by sodium monochloroacetate leads to the formation of a polyelectrolyte with the structure of a polycomplexone.

THERMOOXIDATIVE DEGRADATION OF POLYPROPYLENE—III. INVESTIGATION OF THE COMPLETE EFFECTIVENESS OF SOME ANTIOXIDANTS

Yu. A. Shlyapnikov, V. B. Miller, M. B. Neiman, E. S. Torsueva and B. A. Gromov, Vysokomol. soedin. **2**: No. 9, 1409—1413, 1960.

A study has been made of the thermooxidative degradation of polypropylene in the presence of some antioxidants. The most active of those studied (ionol, propylgallate, "Neo-

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zone D" and diphenyl-*p*-phenylenediamine) prolong the induction period of polypropylene oxidation by over 70 times at an antioxidant concentration 0·01 mole/kg and temperature 140°C.

POLYMERIZATION OF MONOMERS IN SWELLING COPOLYMERS

E. B. Trostyanskaya, A. S. Tevlina and I. P. Losev, Vysokomol. soedin. **2**: No. 9, 1413—1418, 1960.

THE possibility of lac polymerization of monomers in polymers limitedly swelling in the selected solvent has been investigated. In all cases it has been found that a stable insoluble copolymer—polymer system forms. This gives grounds to the belief that polymerization of a monomer in a polymer swelling in the former is accompanied by grafting, owing to the increased possibility of chain transfer under such conditions to the polymer. The method has been used to increase the concentration of ionogenic groups in insoluble polyelectrolytes (ion exchangers) by polymerization, for instance, of methacrylic or vinylsulphoacids in the granules of a sulphonated copolymer of styrene and divinylbenzene or methylvinylpyridine in a copolymer of the vinylbenzyltrimethylammonium base and divinylbenzene. Also with the aid of this method polymethacrylic acid and polymethylvinylpyridine have been grafted on to films of limitedly swelling polyvinylalcohol and hydrocellulose.

MODIFIED INSTRUMENT FOR THE MEASUREMENT OF LIGHT SCATTERING IN SOLUTIONS OF POLYMERS AND PROTEINS

V. Ya. Chernyak, Vysokomol. soedin. **2**: No. 9, 1419—1425, 1960.

THE most important parts of the well known instrument for comparative light scattering measurements employing a Pulfrich photometer, namely, the measuring cell and its thermostat and the "reference line", have been modified. This led to improvement of the sensitivity and the accuracy and reproducibility of its results as well as to simplification of some of the laborious ancillary operations without making the apparatus more involved. By a sufficiently strict account of the specific features of the visual instrument a simple formula has been obtained for calculating R_{90}, containing only one "correction" factor n^2. Simplified procedures for adjusting the instrument and for its calibration have been described. Results of test measurements of R_{90} for H_2O and CCl_4 as well as of determinations of the molecular weight of human γ-globulin have been presented.

STUDIES IN THE MECHANOCHEMISTRY OF POLYMERS—X. INITIATION OF POLYMERIZATION BY RADICALS FORMED IN THE ULTRASONIC DEGRADATION OF MACROMOLECULES

A. A. Berlin and A. M. Dubinskaya, Vysokomol. soedin. **2**: No. 9, 1426—1431, 1960.

POLYMERIZATION of the monomers is observed in the degradation of polymethylmethacrylate in styrene, methylmethacrylate and acrylonitrile by the action of ultrasonic radiation at an intensity level of 7–48 Wt/cm² and frequency of 1500 kc/s. A block-grafted copolymer has been isolated in the case of ultrasonic radiation of polymethylacrylate in acrylonitrile, and its properties have been investigated.

CARBOCHAIN POLYMERS AND COPOLYMERS—XXVII. POLYMERIZATION AND COPOLYMERIZATION OF DI-*n*-BUTYL VINYLPHOSPHINATE

H. S. Kolesnikov, E. F. Rodionova, L. S. Fedorova and L. A. Gavrikova, Vysokomol. soedin. **2**: No. 9, 1432—1437, 1960.

THE polymerization of di-*n*-butyl vinylphosphinate by different methods has been inves-

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tigated and it has been found that the highest molecular weight compound (MW = 9500) is obtained in polymerization by the molecular beam method in the presence of magnesium. The thermomechanical properties of the polymers have been shown to change with increasing molecular weight from 1300 to 9500. Copolymers of di-*n*-butyl vinylphosphinate with styrene have been obtained and the thermomechanical properties of the polymers of various composition have been determined. Copolymers have also been obtained of vinyl chloride and styrene. Polymerization takes place if monomeric di-*n*-butyl vinylphosphinate is irradiated with fast electrons. Radiation by fast electrons of poly-di-*n*-butyl vinylphosphinate leads to the formation of a three-dimensional, insoluble product.

BRITTLE FRACTURE OF POLYMERS IN THE HIGH ELASTIC STATE

G. A. Patrikeev, B. G. Gusarov and V. L. Konoplev, Vysokomol. soedin. **2**: No. 9, 1438—1439, 1960.

THE strength of rubber specimens weakened by incision greatly diminishes on tests in the range of -20 ± 5°C during stretching velocities greater than 0·7 m. sec^{-1}. The weakening effect is interpreted as the result of brittle fracture due to a rise in the glass temperature resulting from the assumed considerable deformation rates in the mouth of the incision.

DETERMINATION OF THE STRUCTURAL GLASS TRANSITION TEMPERATURE FROM EXPERIMENTAL CURVES

Yu. A. Gorbatkina, Vysokomol. soedin. **2**: No. 10, 1456—1458, 1960.

THE relation between the structural glass transition point of Volkenshtein and Ptitsyn's theory and the experimental one has been examined. It has been shown that the glass transition point determined as the point of intersection between the linear heat expansion curves for the solid and liquid states does not coincide with the theoretical value. The theoretical glass transition point may be determined from a plot of the temperature hysteresis of the volume. By a comparison of the temperatures determined from the intersection of the straight lines and the theoretical value one may determine the structural relaxation time at $T = T_g$.

THE GAMMA-RAY INDUCED GRAFTING OF SOME POLYMERS ON TO NATURAL SILK AND CAPRON

S. A. Azimov, Kh. U. Usmanov, N. V. Kordub and S. I. Slepakova, Vysokomol. soedin. **2**: No. 10, 1459—1462, 1960.

GRAFTING of acrylonitrile and styrene on to natural silk and capron has been accomplished by irradiating the polymer immersed in a solution of the monomer. The optimal conditions for the grafting process have been established. Analysis of the infrared absorption spectra indicates that the CN-group has been incorporated in the silk and capron; the hydrogen bonds of the groups —CO—NH— being preserved. It has been shown that as a result of irradiation of silk in air breakdown of the main fibroin chain and loss in packing density of the macromolecules take place.

ORGANOSILICON ESTERS OF ACRYLIC AND METHACRYLIC ACID — II. POLYMERIZATION AND THE PROPERTIES OF THE POLYMERS

B. N. Dolgov†, E. V. Kukharskaya and D. N. Andreev, Vysokomol. soedin. **2**: No. 10, 1463—1465, 1960.

† *Deceased*

It has been shown that organosilicon esters of acrylic and methacrylic acid are capable of polymerization under the action of peroxide catalysts and ultraviolet light with the

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formation of the rubber-like or solid, transparent and colourless polymers. The properties of the polymers have been determined. The polymers with a three-dimensional structure have been found to possess high softening temperatures. All the polymers are easily hydrolyzed by water. The polymer obtained from triacyloxysilanes is water soluble.

THERMOCHEMICAL ASSESSMENT OF THE STRUCTURAL PROPERTIES OF POLYMERIC MATERIALS

B. E. Geller, Vysokomol. soedin. **2**: No. 10, 1466—1469, 1960.

A METHOD for assessing the structural properties of polymeric materials has been proposed, based on the rate of evolution of heat during swelling of the high molecular compounds. It has been found that the intensity of the heat flux arising on diffusion of the solvent into the material may serve as characteristic of the structural density. This new characteristic of the density of the molcular structure has been termed "the coefficient of heat evolution I". The molecular structure density characteristics of carbochain fibres prepared have been presented.

DETERMINATION OF COHESION ENERGY DENSITIES OF SOME SYNTHETIC RUBBERS

V. E. Basin and A. G. Shvartz, Vysokomol. soedin. **2**: No. 10, 1470—1474, 1960.

THE cohesion energy densities of the rubbers SKS-30A, SKS-30ShKhP, SKM-5tr, SKMVP-15A, SKD-1, SKS-30-1 have been determined. It has been shown that pyridine and carboxyl groups impart different properties to the polymers. In the amounts investigated carboxyl groups raise the cohesion energy, but have little effect on the rubber-solvent interaction, whereas pyridine groups practically leaving the cohesion energy unchanged, have a strong influence on the nature of interaction between the rubber and the solvent.

COPOLYMERIZATION OF UNSATURATED POLYESTERS WITH VINYL AND ALLYL MONOMERS — XI. COPOLYMERIZATION OF POLYDIETHYLENEGLYCOLFUMARATEADIPINATE AND OF LOW MOLECULAR POLYETHYLENEGLYCOLFUMARATE WITH STYRENE

S. S. Spasskii and T. V. Molchanova, Vysokomol. soedin. **2**: No. 10, 1481—1485, 1960.

THE copolymerization of polyethyleneglycolfumarateadipate and of low molecular polydiethyleneglycolfumarate with styrene has been investigated. The relative reactivity ratios of polydiethyleneglycolfumarate and polyethyleneglycolfumarateadipate were found to posses close values. When the molecular weight of the polyester is considerably lowered the activity of styrene in the copolymerization reaction with unsaturated polyesters increases, approaching that of styrene in reactions with diesters of fumaric acid.

SORPTION OF THE ORGANIC ANION OF THE DYE 1 (2′ 4′-DIMETHYLPHENYLAZO)-2-OXYNAPHTHYL 3,6-DISULPHONIC ACID ON THE WEAKLY BASIC ANION EXCHANGER AN-15

G. S. Libinson, E. M. Savitskaya and B. P. Bruns, Vysokomol. soedin. **2**: No. 10, 1500—1507, 1960.

THE sorption of the anion of the dye 1(2′,4′-dimethylphenylazo)-2-oxynaphthyl 3,6-disulphonic acid on the OH, Cl and SO_4 forms of the weakly basic anion exchanger AN=15

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has been investigated. The presence of pseudoequilibria has been demonstrated and confirmed by observations on the distribution of the dye in the bulk of the grain. The sorption of the dye on AN-15 from hydrochloric acid solutions of various concentration has been elucidated. Sorption of the dye on the SO_4 form of the exchanger takes place only in the surface layer of the particles, owing to the low diffusion rate of the large anion in the sulphate form of the resin.

POLYMERIZATION OF OCTAMETHYLCYCLOTETRASILOXANE IN THE PRESENCE OF TIN TETRACHLORIDE

K. A. Andrianov and S. E. Yakushkina, Vysokomol. soedin. **2**: No. 10, 1508–1511, 1960.

It has been shown that on interaction between octamethylcyclotetrasiloxane and stannic chloride at temperatures above 100° ring cleavage takes place, linear polymers being formed. As a result of the polymerization soluble products are obtained with a mean molecular weight of about 350,000. The polymerization rate increase with increase in catalyst concentration and with elevation of the polymerization temperature. The glass transition temperature of the polymer is the same as that of a specimen of polydimethylpolysiloxane rubber of the same molecular weight. It has been suggested that polymerization of octamethylcyclotetrasiloxane under the influence of stannic tetrachloride proceeds through formation of an intermediate active complex with the latter.

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EFFECT OF THE PHASE STATE OF POLYETHYLENE DURING IRRADIATION ON THE NATURE OF THE NETWORK FORMED

G. P. Ushakov, Yu. A. Guscho, Yu. S. Lazurkin, and V. S. Kazakov. Vysokomol. soedin. **2**: No. 10, 1512–1520, 1960.

The effect of the phase state of polyethylene during irradiation on the nature of the network formed has been investigated. For equal mean densities of the network, its influence on the melting point and on the degree of crystallinity of the irradiated polymer differs sharply for networks formed on irradiation of polyethylene in the crystalline or amorphous states. On irradiating polyethylene in the crystalline state (45–50°C) the network formed secures the ordered arrangement of the chains in the crystalline formations (spherulites). In addition to breaking down the crystals and lowering the degree of crystallinity such a network enhances the stability of the remaining smaller crystals. Therefore T_m of polyethylene with such a network diminishes little and not monotonously with the dose (network density). The network formed on irradiating polyethylene in the melt (130–160°C) lowers the degree of crystallinity with the dose much faster and completely inhibits crystallization atconsiderably lower doses than in the case of irradiation in the crystalline state; stiff, rubberlike materials being produced.

INVESTIGATION OF THE ELECTROCONDUCTIVITY OF POLYMERS - I. ON THE METHOD OF MEASURING SPECIFIC RESISTANCES OF THE ORDER OF 10^{17}-10^{19} OHM·CM

B. I. Sazhin and V. S. Skurikhina, Vysokomol. soedin. **2**: No. 10, 1535–1540, 1960.

The results are presented of an experimental study of the effect of the design of the specimen, width of the clearance between the guard ring and the electrode h material of the

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electrode and additional annealing of the specimen on the specific resistances Pv of polyethylene and polystyrene. It has been shown that contamination of the surfaces at the clearance and also the use of specimens with $h>0{\cdot}5$ markedly lower the value of Pv.

INVESTIGATION OF THE ELECTROCONDUCTIVITY OF POLYMERS—II. POLYTRIFLUOROCHLOROETHYLENE

B. I. Sazhin and N. P. Stafeeva, Vysokomol. soedin. **2**: No. 10, 1541—1547, 1960.

THE results of an investigation of the electroconductivity of polytrifluorochloroethylene at 15–220 C have been presented. It has shown that below the glass transition temperature the values for the specific resistance of the polymer are basically determined by the polarization currents, whereas for $T>T_g$ by translational conductivity. Three polarization processes have been revealed, discovered earlier with polytrifluorochloroethylene in alternating electrical fields.

EFFECT OF THE STRUCTURE OF POLYESTERS ON THE TEMPERATURE REGION OF DIELECTRIC LOSS MAXIMA

G. P. Mikhailov and M. P. Eidelnant, Vysokomol. soedin. **2**: No. 10, 1548—1551, 1960.

THE temperature frequency function of tanδ of the dielectrical losses of two polyesters, hexamethyleneterephthalate and decamethyleneterephthalate has been presented. The temperatures (max) of the regions of tanδ maxima have been correlated with the structure of the macromolecules of the above and of a number of other polyesters. It has been shown that t_{max} of the dipole-elastic losses depends linearly upon the concentration of the aromatic nuclei in the macromolecular chain. The t_{max} of the dipole-radical losses depends mainly upon the structure of the acid, the value of t_{max} of the dipole-radical losses for polyesters with aromatic acids being higher than for those with aliphatic acids. On the basis of the experimental data it has been concluded that the losses of polyesters are due to relaxation of the COO groups.

INVESTIGATION OF THE DIELECTRIC LOSSES OF POLYETHERS

G. P. Mikhailov and M. P. Eidelnant, Vysokomol. soedin. **2**: No. 10, 1552—1556, 1960.

THE temperature-frequency relations of tanδ of the dielectrical losses of polyoxymethylene and polyxylylenoxyd have been presented. Two superimposing regions have been observed in the case of polyoxymethylene, namely, dipole-elastic and dipole-radical losses. With polyxylylenoxyd there are two regions of dipole-radical and one of dipole-elastic losses.

The temperatures of the regions of maximum tanδ have been correlated with the structure of the polyethers. It has been shown that the dipole-radical losses are caused by relaxation of the ether groups, the dipole-elastic one by segmental motion of the chains.

STUDIES IN THE SERIES OF CHELATE POLYMERS—I. SYNTHESIS OF CHELATE POLYMERS ON THE BASE OF 5,5-METHYLENE-BIS-SALICYL ALDEHYDE

A. P. Terentev, V. V. Rode and E. G. Rukhadze, Vysokomol. soedin. **2**: No. 10, 1556—1563, 1960.

A DESCRIPTION has been presented of the synthesis of 23 chelate polymers of copper, nickel, zinc, cadmium, cobalt and iron with poly-5,5′methylene-bis-salicylalimine, poly-5,5′-met-

hylene-bis-salicylalethylendiimine, poly-5,5′-methylene-bis-salicylalhexamethylendiimine and poly-5,5′-methylene-bis-phenylenediimine as well as the synthesis of the polymeric Schiff bases 5,5′-methylene-bis-salicyl aldehyde with ethylenediamine, hexamethylenediamine and *o*-phenylenediamine. An improved method for the synthesis of 5,5′methylene-*bis*-salicyl aldehyde with a yield 75% of the theoretical has been developed.

INVESTIGATION OF POLYMER-FILLER INTERACTION — I. ON THE CHANGE IN PROPERTIES OF SOME POLYMERS ATTACHED TO A GLASS SURFACE

Yu. S. Lipatov and G. M. Pavluchenko, Vysokomol. soedin. **2**: No. 10, 1564—1568, 1960.

A STUDY has been made of the swelling of thin gelatine and polystyrene films and of the same films applied to a glass fiber surface. It has been shown that the degree of swelling of gelatine on the surface is lowered in comparison with the free gelatine whereas in the case of polystyrene it is augmented. A fall in the glass transition temperature of polystyrene from 80·4° for the free polymer to 74·6° for that on the glass surface has also been found to take place. Based on the results it has been concluded that there is a significant change in properties of polymers in the form of thin films on the surface. This is due to interaction of the glass surface with the packets of molecular chains.

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INVESTIGATION OF POLYMER-FILLER INTERACTION — II. ADSORPTION OF POLYMERS FROM SOLUTION BY GLASS FIBRES

Yu. S. Lipatov, L. M. Sergeeva and V. P. Maksimova, Vysokomol. soedin. **2**: No. 10, 1569—1574, 1960.

THE adsorption by glass fibre of polystyrene from solutions of concentration up to 3% in the case of a good solvent benzene and of a poor solvent cyclohexanone, and of polymethylmethacrylate from acetone and from toluene has been investigated. In the polymethylmethacrylate from acetone and from toluene has been investigated. In the case of polystyrene no adsorption of the polymer from the poor solvent has been observed at 25° and in the case of polymethylmethacrylate, no adsorption from the poor solvent took place at any of the temperatures investigated. The nature of adsorption from concentrated solutions has been shown to differ from that from dilute solutions. This is due to the transition of molecular associates to the glass fibres during the adsorption prosess in concentrated solutions, rather than of individual macromolecules.

PREPARATION OF SOME GRAFT COPOLYMERS BY OZONIZATION

P. V. Kozlov, M. M. Iovleva, A. Kh. Khakimova and A. Zezin, Vysokomol. soedin. **2**: No. 10, 1574—1579, 1960.

THE method of ozonization has been applied to the preparation of graft copolymers from polystyrene and vinyl acetate, polyisobutylene and styrene, and polyethyleneterephthalate and acrylic acid. It has been shown that the graft copolymer from the system polystyrene—vinylacetate is produced with the least amount of the grafted-on part (polyvinylacetate) as compared with the other systems.

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SOLUBILITY OF SOME GRAFT COPOLYMERS

P. V. Kozlov, M. M. Iovleva, A. Kh. Khakimova, A. Zezin and A. Klushina, Vysokomol. soedin. **2**: No. 10, 1580—1585, 1960.

On the basis of studies of the state diagrams of the diphenyl type of graft copolymers (starch-polystyrene, polyethyleneterephthalate-polyacrylic-acid) and of the copolymers of which the initial components have a common solvent (polystyrene-polyvinylacetate, polyisobutylene, polystyrene) it has been suggested that the act of grafting as a rule causes a loss in the true solubility of the graft copolymer as compared with the initial homopolymers.

Comparison of the integral heats of swelling of the polystyrene-polyvinylacetate graft copolymer in benzene and in a mixture of hydrogenated monomers with a mechanical mixture of the polymers in the hydrogenated monomers, as well as with polystyrene in benzene clearly demonstrated an increase in on dissolution of the graft copolymer. This shows that as a result of the grafting, loosening of the chain packing took place. At the same time the sharp decrease in solubility of graft copolymer is explained by an increase in the negative entropy effect.

The data obtained have been discussed in the light of the thermodynamic data on solubility of polystyrene-polyacrylic acid copolymer obtained by us earlier.

SYNTHESIS OF LINEAR POLYMERS OF THE GLYCIDYL ESTERS OF UNSATURATED ACIDS BY THE CYCLIC POLYMERIZATION MECHANISM

I. A. Arbuzova and V. N. Efremova, Vysokomol. soedin. **2**: No. 10, 1586—1587, 1960.

Up to the present time the reaction of cyclic polymerization has been known for diolefinic monomers. On the example of the polymerization of the glycidyl esters of the unsaturated acrylic and methacrylic acids effected by ionic catalysts we have discovered a new case of cyclic polymerization taking place through interand intramolecular polymerization at the double bond and the α-oxide ring.

EQUATIONS FOR THREE COMPONENT COPOLYMERS—I

A. I. Tarasov, V. A. Tskhai and S. S. Spasskii, Vysokomol. soedin. **2**: No. 11, 1601—1607, 1960.

Equations for the composition of three component copolymers have been investigated with the objective of establishing criteria for the existence of azeotropic systems. A correlation has been found between he monomer reactivity ratios of binary mixtures for which an azeotropic composition of three component vinyl polymer systems is possible. It has been shown that the three component system can have only one azeotropic composition.

THE STRUCTURE OF REINFORCED BUTADIENE-NITRILE RUBBER VULCANIZATES BY THE SOFTENING-ELONGATION RELATION

V. A. Shvetsov, A. S. Novikov and A. P. Pisarenko, Vysokomol. soedin. **2**: No. 11, 1608—1612, 1960.

The effect of preliminary stretching of rubbers with SKN-26 base and channel black or aluminum hydroxide fillers on the stress-strain curves has been shown. On the basis of the Blanchard-Parkinson equation: $\ln F - f(\alpha) = \ln G + \mu(\alpha - 1)^4$ where F is the stress per unit area of the initial cross section, α the coefficient of elongation, q the modulus (proporti-

onal to the number of links in the vulcanizate), and μ a factor, characterizing the degree of interaction between the rubber and filler. It has been shown that vulcanizates containing aluminum hydroxide are subjected to greater softening during elongation than those containing the channel black.

COMMENTS ON THE CRYSTAL STRUCTURE OF POLYACRYLONITRILE

Z. Mencik, Vysokomol. soedin. **2**: No. 11, 1635—1638, 1960.

THE crystal structure of polyacrylonitrile previously held to be hexagonal has been examined by X-ray diffraction. The hexagonal structure is unacceptable bon several grounds. Owing to a poorly defined diffraction pattern (weak reflections and virtual absence of clear reflections other than equatorial) the structure can hardly be interpreted at present with certainty. The defective structure is believed to be due to irregularities in the position of the CN substituents with respect to the C-C backbone of the polymer. An orthorhombic elementary cell is tentatively proposed, which satisfies the observed reflections and the polymer density.

SYNTHESIS AND POLYMERIZATION OF UNSATURATED ORGANOMETALLIC COMPOUNDS

M. M. Koton, T. M. Kiseleva and F. S. Florinskii, Vysokomol. soedin. **2**: No. 11, 1639—1644, 1960.

THE following unsaturated organometallic monomers have been synthesized for the first time: methacrylate (acrylate) triphenyllead, methacrylate (acrylate) phenylmercury, acrylate triphenyltin, *p*-phenylmercurystyrene, *bis*-(paravinylphenyl)mercury, *p*-triphenylplumbylstyrene. The monomers easily polymerize and copolymerize with vinyl monomers. Metal-containing styrenes polymerize more rapidly than the corresponding metal-containing methacrylates. The polymers are technically stable compounds.

INVESTIGATION OF INTERFACIAL POLYESTERIFICATION

I. P. Losev, O. V. Smirnova, O. G. Fortunatov and A. D. Neklyudov, Vysokomol. soedin. **2**: No. 11, 1659—1664, 1960.

A NUMBER of factors affecting the interfacial polyesterification of dian and terephthalyl chloride has been investigated. The molecular weight and yield of the polyester have been studied as functions of the concentrations of the solutions of reagents, of the temperature, of the stirring time and of the amount of alkaline agent.

Several aromatic and arylaliphatic polyesters have been synthesized from adipyl, sebacyl and terephthalyl chlorides. The film forming capacity of the polymers has been investigated. A copolymer has been synthesized from 4,4′-dihydroxydiphenyl-1,1-cyclohexane and adipyl and terephthalyl chlorides.

SYNTHESIS AND INVESTIGATION OF THE PRODUCTS OF INTERACTION BETWEEN 4,4′-DIHYDROXYDIPHENYL-2,2-PROPANE AND DIPHENYLCARBONATE

I. P. Losev, O. V. Smirnova and E. V. Smurova, Vysokomol. soedin. **2**: No. 11, 1665—1670, 1960.

POLYCARBONATES have been synthesized by the transesterification method and the effects of various factors on this process (duration of reaction, temperature, catalysts the presence

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of inert gas, and the pressure) have been investigated. Kinetic curves of the reaction have been obtained. The polycarbonates were separated by fractional precipitation.

ADHESION OF POLYMERS—VII. ADHESION OF CARBOXYL-CONTAINING COPOLYMERS TO VARIOUS SUBSTRATES

S. S. Voyutskii, V. L. Vakula, N. I. Smelaya and I. A. Tutorskii, Vysokomol. soedin. **2**: No. 11, 1671—1677, 1960.

THE effect of the content of ionogenic carboxyls in butadienstyrene rubbers (at equal styrene contents) as well as of styrene at equal contents of the polar component (methacrylic acid) on their adhesion to a polar substrate (polyamide) has been investigated. It has been shown that increase of the methacrylic acid content in the copolymers leads to abrupt increase and then abrupt decrease of adhesion to the polyamide, maximum adhesion occurring at a content of 0·3–1·25%. Increase in the styrene content of carboxyl-containing rubbers causes a fall in their adhesion to the polyamide. In all cases elevation of the temperature of heat treatment of the joints strengthens the adhesion. The nature of the substrate on the adhesion of carboxyl-containing rubbers has also been studied. It has been shown that adhesion to polyethylene basically does not depend upon the content of the polar component or of styrene in the copolymers, nor upon the contact temperature. The results have been discussed in terms of the diffusion theory of adhesion.

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ON THE SYNTHESIS OF POLYAMIDES FROM NEUTRAL ESTERS OF DICARBOXYLIC ACIDS AND AROMATIC DIAMIDES

O. Ya. Fedotova and A. S. Kurochkin, Vysokomol. soedin. **2**: No. 11, 1688—1691, 1960.

THE reactions of the diesters of adipic and sebacic acids with metatoluylenediamine have been investigated under varying temperature and time conditions. Polyamides have been obtained with molecular weights from 500 to 4000. They are syrupy compounds or solids with melting points 200°, soluble in both tricresol and concentrated acids as well as in the ordinary organic solvents.

DILATOMETRIC DETERMINATION OF POLYMER-COMPATIBILITY

G. M. Bartenev and G. S. Kongarov, Vysokomol. soedin. **2**: No. 11, 1692—1697, 1960.

THE curves for the linear temperature shrinkage of elastomers permit of a clear cut determination of the compatibility or non-compatibility of polymers, provided their glass transition temperatures are not near each other. Mixtures of non-compatible polymers manifest a number of glass transition temperatures (according to the number of polymers). The values of these temperatures coincide with those for the pure polymers, being independent of the ratio of polymers in the mixture. Mixtures of compatible polymers possess a single glass transition point, varying with change in polymer ratio as a linear function of the concentration by volume. The coefficients of linear expansion (schrinkage) of mixtures from any polymers obey the rule of additivity within the limits of deviation of results from measurements of one sample to another.

INTERNAL STRESSES IN COATINGS—I. METHODS OF CALCULATING INTERNAL STRESSES IN POLYMER AND PAINT AND LACQUER COATINGS

A. T. Sanzharovskii, Vysokomol. soedin. **2**: No. 11, 1698–1702, 1960.

METODS have been proposed for calculating internal stresses in polymer and paint and lacquer coatings: (a) from the curvature of the substratum, (b) from the bending of the free end of a cantilevered substratum, (c) from the value of the stress in the film-free side of the substratum, (d) from the value of the stress in the coated side of the substratum. The methods may be used to calculate the internal stresses appearing in any coatings prepared by single or repeated applications on an arbitrary solid substratum.

INTERNAL STRESSES IN COATINGS—II. EXPERIMENTAL METHODS OF INVESTIGATING THE INTERNAL STRESSES OF POLYMER AND PAINT AND LACQUER COATINGS

A. T. Sanzharovskii and G. I. Epifanov, Vysokomol. soedin. **2**: No. 11, 1703–1708, 1960.

EXPERIMENTAL methods have been developed for investigating the internal stresses of polymers and paint and lacquer coatings. These are: (a) a cantilever method, based on measurement of the free end of a cantilevered substratum, the sensitivity being 0·4 kg/cm², (b) a strain gauge, based on measurement of the internal stresses in the substratum on the film-free side, the sensitivity being 2·0 kg/cm². The methods may be used for the qunatitative determination of internal stresses in polymer and paint and lacquer coatings under varying physicochemical conditions.

INTERNAL STRESSES IN COATINGS—III. INTERNAL STRESSES IN GELATINE AND ACETYLCELLULOSE FILMS APPLIED TO SOLID SUBSTRATUMS

A. T. Sanzharovskii and G. I. Epifanov, Vysokomol. soedin. **2**: No. 11, 1709–1714, 1960.

THE ultimate value of internal stresses in gelatine films is independent of their thickness or of the concentration of the solution from which they were obtained, as well as of the nature of the solid substratum to which they have been applied. With increase in film thickness the elastic force tending to shorten the film and to overcome is adhesion to the substratum increases. For sufficiently thick films cleavage of the bond and separation of the films may take place before the film has completely formed and the stresses have assumed their ultimate values. The real strength of the films falls under the influence of the internal stresses. For gelatine films the fall amounts to 25% and for acetylcellulose to 74%. The internal stresses should have a still greater bearing on the protracted strength of the coatings.

HELICAL STRUCTURES OF POLYETHYLENE

M. B. Konstantinopolskaya, Z. Ya. Berestneva and V. A. Kargin, Vysokomol. soedin. **2**: No. 11, 1715–1716, 1960.

IN contrast to previously described phenomena of ordering in polymers when packets are first formed, followed by planes and with the building up of the planes by crystals, in the present case in more concentrated solutions (0·2%) owing to different mobility of the individual elements of the polymer molecules, helical structures are formed.

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CARBOCHAIN POLYMERS AND COPOLYMERS—XXVIII. PREPARATION OF GRAFT COPOLYMERS BY REACTION BETWEEN POLYMETHYLMETHACRYLATE AND POLYETHYLENEAZELATE

H. S. Kolesnikov and Tsen Khan-min, Vysokomol. soedin. No. 11, 1717–1721, 1960.

GRAFT copolymers have been obtained on reaction between polymethylmethacrylate and polyethyleneazelate. The structure and properties of the copolymers depend not only upon the ratio of the polymers in the initial mixture but also upon the duration of the reaction. On prolonged reaction not only transesterification but also esterolysis takes place, leading to decrease in length of the grafted polyester which changes the properties of the latter.

EFFECT OF STRETCHING ON THE STRUCTURE AND PROPERTIES OF POLYETHYLENETEREPHTHALATE FILMS—III. DIELECTRIC LOSSES OF PLANE ORIENTED FILMS

G. L. Berestneva, L. L. Burshtein, P. V. Kozlov, G. P. Mikhailov and K. E. Nordbek, Vysokomol. soedin. **2**: No. 11, 1739–1743, 1960.

THE function $\tan\delta=\varphi(t°)$ for initially unstretched amorphous polyethylene-terepthalate films and for plane oriented films obtained under various conditions of stretching has been determined at the frequency $f=1000$c/s and temperatures ranging from 20 to 220°.

Based on the properties of this function established by Mikhailov and Sazhin for the amorphous and crystalline states of polymers it has been shown that the plane oriented film stretched at temperatures above the glass transition point (80°C) and subsequently heat treated under stress at the temperature optimum of crystallization of polyethyleneterephthalate (170°C) leads to crystallization of the polymer in primary structures without the formation of spherulites.

SYNTHESIS OF MOLECULAR POLYOXAMIDES BY POLYCONDENSATION AT THE LIQUID–GAS INTERFACE

L. B. Sokolov, L. V. Turetskii and T. V. Kudim, Vysokomol. soedin. **2**: No. 11, 1744–1745, 1960.

IT has been shown that polyoxamides may be prepared by polycondensation of gaseous oxalyl chloride with aqueous solutions of diamines. The yield and intrinsic viscosity of the products obtained in this way are higher than those obtained by polycondensation at the liquid–liquid interface.

POLYMERIZATION OF PROPYLENE IN THE ABSENCE OF SOLVENT

R. Istratoiu, Vysokomol. soedin. **2**: No. 11, 1746, 1960.

IT has been shown that polymerization of propylene in the presence of $AL(C_2H_5)_3+TiCl_3$ at 20 atm. pressure proceeds at higher rate than in the presence of *n*-heptane.

THE EFFECT OF METAL OXIDES ON THE STRUCTURAL TRANSFORMATIONS OF FLUORINATED RUBBER COPOLYMERS UNDER THE ACTION OF IONIZING RADIATION AND HIGH TEMPERATURES

A. S. Novikov, V. L. Karpov, F. A. Galil-Ogly, N. A. Slovokhotova and T. N. Dyumaeva, Vysokomol. soedin. **2**: No. 12, 1761–1767, 1960.

A STUDY of the infrared spectra of fluorine-containing copolymers irradiated in the presence of metal oxides has shown that in contrast to irradiation of the copolymers without

the oxides a considerable number of conjugated double bonds of the type $-CH=CCl-$ is formed in the chain and OH and HF_2^- groups make their appearance. The same changes are undergone by the copolymers in the presence of metal oxides on pressurized heating at 200°. On irradiation of the copolymers in the presence of metal oxides almost no volatile products are evolved, as is the case when irradiation is carried out in the absence of the oxides. From this fact and spectral data one may conclude that both during irradiation and heating of fluoro-copolymers in the presence of metal oxides the latter react with the volatile products evolved. The appearance of bands characteristic of the ion HF_2 indicates the possibility of formation of $Ca(HF_2)_2$. The experimental material suggests that during irradiation of fluoro-copolymers metal oxides play the part of acceptors of hydrogen fluoride and hydrogen chloride, as well as of fluorine, chlorine and hydrogen.

SYNTHESIS OF NEW CELLULOSE AND OTHER POLYSACCHARIDE DERIVATIVES—IX. SYNTHESIS OF THE ESTERS OF CELLULOSE WITH AROMATIC AMINO ACID

Sun Tun, V. A. Derevitskaya and Z. A. Rogovin, Vysokomol. soedin. **2**: No. 12, 1768–1771, 1960.

A METHOD of synthesis of the esters of cellulose with aromatic amino acids has been developed. The esters of cellulose with *p*-nitrobenzoic and *p*-aminobenzoic acids, of various degrees of esterification, have been synthesized for the first time. It has been shown that the esters of cellulose with *p*-aminobenzoic acid may be used in the realization of a new method for obtaining chemically dyed cellulose fibers.

INVESTIGATION OF THE MOLECULAR RELAXATION OF α AND β CHLOROSUBSTITUTED POLYALKYLMETHACRYLATES BY THE DIELECTRIC LOSS METHOD

G. P. Mikhailov and T. I. Borisova, Vysokomol. soedin. **2**: No. 12, 1772–1778, 1960.

EXPERIMENTAL data have been presented on the molecular relaxation of poly-*α* chloroalkylacrylates and polychloroethylmethacrylate by the dielectric loss method. The data have been compared with the results of similar studies zin the series of polyalkylmethacrylates. Conclusions have been made as to the effect of the chlorine atom, replacing the methyl group in the α and β positions, on the relaxation properties of polymers.

EFFECTIVE DIPOLE MOMENTS OF α AND β CHLOROSUBSTITUTED POLYALKYLMETHACRYLATES

G. P. Mikhailov and T. I. Borisova, Vysokomol. soedin. **2**: No. 12, 1779–1785, 1960.

BASED on the temperature and frequency relations of the generalized dielectric constant $\varepsilon=\varepsilon'-i\varepsilon''$ an analysis has been made of the spectrum of relaxation times and the effective dipole moments have been calculated for α and β chlorine derivatives of polyalkylmethacrylates. The results have been compared with analogous data for the homologous series of polyesters of methacrylic acid. The effect of the second polar group on the relaxation properties of the polymer, depending upon the position of the incorporated dipole, has been elucidated.

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DEPENDENCE OF SOLUTION PROPERTIES ON POLYMER STRUCTURE—III. SOLUTIONS OF POLYDIMETHYLSILOXANE

S. R. Rafikov, S. A. Pavlova and I. I. Tverdokhlebova, Vysokomol. soedin. **2**: No. 12, 1786–1793, 1960.

THE properties of chlorobenzene, benzene and iso-octane solutions of polydimethylsiloxane have been investigated. Measurements have been made of the viscosity, molecular weight and coefficients of diffusion and sedimentation. The following equations have been established for polydimethylsiloxane in chlorobenzene: $[\eta]_{\theta,25^\circ} = 3{\cdot}72 \times 10^{-4} M^{0{\cdot}72}$; $[\eta]_{30^\circ} = 2{\cdot}24 \times 10^{-4} M^{0{\cdot}74}$; $[\eta]_{40^\circ} = 0{\cdot}793 \times 10^{-4} M^{0{\cdot}66}$ = and in benzene $[\eta]_{\theta,25^\circ} = 2 \times 10^{-4} M^{0{\cdot}78}$ $[\eta]_{40^\circ} = 2{\cdot}04 \times 10^{-4} M^{0{\cdot}80}$.

With change in temperature and solvent the constant $A = \eta_0 T^{-1} D(M[\eta])^{1}/_{3}$ changes within the limits $2{\cdot}27 \times 10^{-10}$ to $2{\cdot}8 \times 10^{-10}$ erg/deg. It has been shown that for polydimethylsiloxane solutions the dependence between the molecular weight and viscosity obeys the earlier proposed equation

$$[\eta] = \frac{21}{37}\left(\frac{1}{2500 \times 37} \cdot M\right)^{a}$$

The root mean square distances between the chain ends for polydimethylsiloxane in chlorobenzene and benzene and for the "unperturbed" coil have been calculated. These have been shown to coincide with the values for $(h_0^2)_\varphi^{\frac{1}{2}}$ calculated for an ideal solvent.

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SYNTHESIS AND POLYMERIZATION OF N-ALLYLLACTAMS

M. F. Shostakovskii, F. P. Sidelkovskaya and F. I. Kolodkin, Vysokomol. soedin. **2**: No. 12, 1794–1800, 1960.

THE compounds N-allyl-2-pyrrolidone, N-allyl-ε-caprolactam and N-allyl-α-piperidone have been synthesized and described. In a study of the polymerization of N-allyl-pyrrolidone and N-allylcaprolactam in the presence of free radical initiators it was found that N-allyllactam is not activated by benzoyl peroxide, but with 5–10% azoisobutyrodinitrile it undergoes stepwise polymerization to produce low yields of the dimers and trimers. The copolymerization of N-allylpyrrolidone with vinyl acetate, methyl methacrylate and methyl acrylate has been investigated.

THE WELDING OF TEFLON AND OTHER POLYMERIC MATERIALS BY THE LOCALIZED ACTION OF NEUTRON RADIATION

I. M. Barkalov, V. I. Goldanskii, B. G. Dzantiev and E. V. Egorov, Vysokomol. soedin. **2**: No. 12, 1801–1804, 1960.

THE welding of materials by irradiation with heat neutrons has been effected according to a method in which the ionizing radiation is localized with the aid of boron and lithium compounds applied to the surfaces subjected to the welding process. The efficiency of the method is characterized by the coefficient of localization of the radiation effect, equal to the ratio of the dose emitted in the bulk.

The radiation welding of the following pairs of polymers has been carried out: teflon-polystyrene, teflon-polymethylmethacrylate, polystyrene-polymethylmethacrylate, polyethylene-polystyrene and polyethylene-polymethylmethacrylate.

The tensile strength of the function for the teflon-polystyrene pair attains a value of 120 kg/cm². Possible mechanisms of the welding reaction have been discussed and some quantitative evaluations have been presented.

By using as intermediate layer polystyrene films containing lithium or boron compounds, three layer welding of polyethylene and teflon was achieved, both with each other, as well as with other polymeric and non-polymeric materials.

SPECTROSCOPIC STUDY OF CELLULOSE-ETHERS. I. ON THE APPLICABILITY OF SPECTRAL METHODS TO CHARACTERIZE THE PHOTOCHEMICAL REACTIONS OF ETHYLCELLULOSE

M. A. Katibnikov, I. N. Ermolenko, A. I. Somova, O. G. Efremova and S. A. Glikman, Vysokomol. soedin. **2**: No. 12, 1805–1810, 1960.

THE ultraviolet, infrared and luminescence spectra of ethylcellulose preparations with varying carboxyl group contents have been investigated. The luminescence spectra and intensities have been found to change as the preparations are irradiated with ultraviolet light. The changes are particularly marked in the initial steps of irradiation, thus allowing one to assert the very first stages of degradation of ethylcellulose molecular chains. Light sensitivity has been shown to increase with the carboxyl content of the ethylcellulose specimens. Neutralization of the groups by Pd and Na cations leads to light stabilization of the compounds. It has been suggested that the presence of carboxyl groups in the ethylcellulose compounds accelerates the ultraviolet induced photochemical reactions. This is in accord with the earlier expressed assumption on the part played by carboxyl groups in the thermo-oxidative degradation of ethylcellulose.

SYNTHESIS AND PROPERTIES OF METHYLMETHACRYLATE-DIMETHACRYLAMIDO-DIMETHYL ETHER COPOLYMERS

I. A. Arbuzova, V. N. Efremova and A. G. Eliseeva, Vysokomol. soedin. **2**: No. 12, 1828–1831, 1960.

COPOLYMERS have been prepared of methylmethacrylate and the dimethacrylamidodimethyl ether had been synthesized by us for the first time. In order to investigate the influence of crosslinking copolymers containing up to 15 mole% dimethylacrylamidodimethyl ethers were produced and their properties investigated. It has been shown that the crosslinking reaction may be effectively made use of within a certain region of low (up to 5 mole%) additions of the diolefine comonomer, wherein there is an improvement in the mechanical properties of the copolymer. Further increase in crosslinking causes a fall in the strength characteristics, the glass transition temperature continuing to rise.

PREPARATION OF POLYETHYLENOXIDES BY POLYMERIZATION OF ETHYLENE OXIDE

M. Kh. Gluzman, B. I. Dashevskaya and V. M. Bodnya, Vysokomol. soedin. **2**: No. 12, 1832–1838, 1960.

TWO methods of synthesizing polyethyleneoxides have been developed, namely polymerization of ethylene oxide in the liquid phase under pressure, and bubbling gaseous ethylene oxide through alkaline solutions of the lower glycols. Both methods permit products to be obtained of various degree of polymerization, from liquids to waxlike solids. The principal factor determining the properties of the polymers is the molar ratios of ethylene oxide: glycol and ethylene oxide:water. Naturally, the more the number of ethylene oxide molecules combines with a glycol molecule the greater the molecular weight and the higher the melting

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point. The maximum value for the molecular weight of the polymer is determined by the nature of the catalyst and the degree of purity of the monomer. The catalyst concentration affects the properties of polyethyleneoxide only at very low values of the former. The polymerization rate of the pressurized liquid reaction is determined by the temperature, catalyst concentration and conditions of contact between the monomer and catalyst. The polymerization rate in the column type of apparatus decreases with increase in molecular weight of the polymer and decrease in catalyst concentration. Two methods of purification of technical polyethyleneoxide have been investigated by means of ion exhangers and electrodialysis. It has been shown that the reaction may be halted at any stage and then resumed by re-establishing the reaction conditions.

IS BORIC ANHYDRIDE A POLYMER?

G. M. Bartenev and A. S. Eremeeva, Vysokomol. soedin. **2**: No. 12, 1845–1849, 1960.

THE mechanical properties of glassy boric anhydride have been investigated above and below the glass transition temperature. In its mechanical properties glassy boric anhydride is similar to both organic polymers and disperse systems. Softened glassy P_2O_5 below the yield point is in a high elastic state of the same type as with organic polymers; above the yield point Newtonian flow is observed. These facts indicate that glassy boric anhydride is a linear inorganic polymer with relatively short chains, explaining the relatively low yield value and narrow temperature range of high elasticity. This is propably also the explanation of the similarity between the rheological curves of boric anhydride and disperse systems.

INVESTIGATION OF THE MECHANISM OF OXYGEN OXIDATION OF CELLULOSE ETHERS – VII

V. I. Kurlyankina, A. B. Polyak and O. P. Kozmina, Vysokomol. soedin. **2**: No. 12, 1850–1853, 1960.

OXIDATION of ethylcellulose by oxygen leads to the formation of ester groups in the macromolecule. The CO absorption band in the infrared absorption spectrum of oxidized ethylcellulose has been resolved with the aid of a fluorite prism and frequencies characteristic of ketone, aldehyde, carboxyl and ester groups have been established.

EFFECT OF STRETCHING ON THE STRUCTURE AND PROPERTIES OF POLYETHYLENETEREPHTHALATE FILMS – IV. INVESTIGATION OF THE MACROSTRUCTURE OF THE STRETCHED FILMS BY MEANS OF ETCHING

G. L. Berestneva and P. B. Kozlov, Vysokomol. soedin. **2**: No. 12, 1854–1859, 1960.

THE microstructure of polyethyleneterephthalate films subjected to various kinds of stretching and crystallized by heat treatment has been investigated by the ething method. Ething pictures of uniazially, biazially and multiazially stretched crystallized films characterizing their microstructures have been obtained and discussed.

CARBOCHAIN POLYMERS AND COPOLYMERS. – XXIX. SYNTHESIS OF DIPHILIC GRAFT COPOLYMERS

Tsen Khan-min and H. S. Kolesnikov, Vysokomol. soedin. **2**: No. 12, 1870–1875, 1960.

IT has been shown that graft copolymers of the diphilic type may be produced by heating mixtures of methacrylic and ω-hydroxypelargonic acids or of methacrylic acid and poly-

hydroxypelargonate in the presence of *p*-toluenesulphonic acid. The properties of the resultant graft copolymers in relation to their composition have been investigated. The presence of spherulites has been revealed in the copolymers.

ESTIMATION OF THE MOLECULAR WEIGHT DISTRIBUTION OF POLYCARBONATES BY THE METHOD OF TURBIDIMETRIC TITRATION

S. Krozer, M. Vainryb and L. Silina, Vysokomol. soedin. **2**: No. 12, 1876–1881, 1960.

THE procedure of determining the physical polydispersity, i. e. molecular weight distribution, of polycarbonates by turbidimetric titration has been described. The conclusion was drawn that the size of the deposited polycarbonates aggregates on adding a precipitant to dilute solutions of the polymer is independent of the molecular weight of the polycarbonates.

THE POSSIBILITY OF HARDENING UNSATURATED POLYESTERS BY TITANIUM TETRACHLORIDE

T. E. Lipatova, Vysokomol. soedin. **2**: No. 12, 1882, 1960.

IT has been found that titanium tetrachloride may cause the hardening of polydiethyleneglycolmaleate with styrene and of polyacrylate esters.

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SYNTHESIS OF SOME EPOXIDE RESINS

V. D. Yasnopolskii and A. A. Medzhidov, Vysokomol. soedin. **3**: No. 1, 3–6, 1961.

EPOXIDE resins have been synthesized by reacting epichlorohydrin with resorcinol and phoroglucinol. No polymerization was observed during reaction of epichlorohydrin with thiobenzamide. By the reaction of epichlorohydrin with hydrazine it has been shown that the presence in the reactants of a benzene ring facilitated the formation of solid, fusible or infusible polymers.

THE ACTION OF MAGNESIUM ON *p*-XYLYLENE DIBROMIDE

V. D. Yasnopolskii and A. A. Medzhidov, Vysokomol. soedin. **3**: No. 1, 7–9, 1961.

ON the basis of a study of the reaction between magnesium and *p*-xylylene dibromide it has been found that the principal product of the reaction is a polymer of the structure: $BrMg(-CH_2-C_6H_4-CH_2-)_{50}MgBr$. The polymer is a non-melting yellow powder, insoluble in organic solvents.

COMPOSITION EQUATIONS FOR THREE-COMPONENT COPOLYMERS—II

A. I. Tarasov, V. A. Tskhai and S. S. Spasskii, Vysokomol. soedin. **3**: No. 1, 14–20, 1961.

THE copolymer equation for three-component molecules of azeotropic compositions has been shown capable of representation in the form of a hyperbola. It has been found that the position of the hyperbolas in the M_1, M_2 coordinate system is determined by the relation between the monomer reactivity ratios. If the relation is such that the hyperbolas lie in the first coordinate quadrant the set of values of M_1 and M_2 included within the hyperbola

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intercepts is a region of approximate azeotropic compositions. Criteria have been presented for the dimensions of the region. A method of plotting the region on a triangular diagram has been proposed.

CHEMICAL CONVERSIONS OF POLYMERS—IV. THERMO-OXIDATIVE REACTIONS OF POLYAMIDES

S. R. Rafikov and R. A. Sorokina, Vysokomol. soedin. **3**: No. 1, 21–29, 1961.

THERMO-OXIDATIVE reactions of polyamides of various compositions and structures have been studied in the solid and liquid states over a wide range of temperatures.

It has been found that polyamide films and fibres with their large surface contact with air are easily subjected to thermo-oxidative ageing at 140°C and higher. The over-all effect of the thermo-oxidative reactions leads to formation of branched and also three-dimensional "supermolecular" structures with deterioration of the mechanical properties and insignificant changes in chemical composition. The reaction takes place according to the radical-chain mechanism through peroxide intermediates formed at temperatures above 80°. The oxidation rate depends upon the orientation of the polyamide. In the high temperature thermo-oxidation of molten polyamides the reaction is limited by diffusion of oxygen, owing to which the formation of oxidation products is of a local character.

The high temperature oxidation products are insoluble, non-melting compounds that do not swell in cresol. The mechanism of their formation has been discussed. Separate steps of the mechanism suggested have been previously checked on low molecular model compounds. At high temperatures alongside oxidation, thermal structuration and degradation processes take place, the nature of which depends upon the structure of the polyamide. These reactions proceed by an exchange and heterolytic mechanism.

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SPECTROSCOPIC STUDY OF CELLULOSE ETHERS—II. INVESTIGATION OF THE THERMAL AND LIGHT STABILITIES OF ETHYLCELLULOSE

I. N. Ermolenko, M. A. Katibnikov and A. I. Somova, Vysokomol. soedin. **3**: No. 1, 30–32, 1961.

THE absorption and luminescence spectra of ethylcellulose preparations differing in their oxidized low molecular fraction contents have been studied before and after thermal treatment or ultraviolet irradiation. It has been shown that the thermal and light stabilities of ethylcellulose depend to a considerable degree upon its content of oxidized low molecular fractions.

CHANGES IN THE MOLECULAR PACKING DENSITY OF CARBOCHAIN POLYMERS

B. E. Geller, Vysokomol. soedin. **3**: No. 1, 33–36, 1961.

THE specific gravity has been determined of carbochain polymers subjected to stretching and thermorelaxation. It has been shown that the molecular packing density depends upon the orientation and thermorelaxation. A theoretical calculation has been made of the specific gravity of a number of the polymers.

FILLED POLYMERS—IV. COMPOUND OF DISSOLVED POLYMETHYLMETHACRYLATE WITH FILLERS

I. A. Uskov, Yu. G. Tarasenko and T. A. Kusnitsyna, Vysokomol. soedin. **3**: No. 1, 37–40, 1961.

EMPLOYING organic bentonite derivatives and polymethylmethacrylate as example a method has been developed for incorporating a filler into a polymer in the dissolved state with subsequent coprecipitation of both components. According to data of differential thermo-

graphic analysis this leads to dense screening of the filler surface by macromolecules of the polymer, i. e. to compatability of the components. The strength of the resultant filled polymer in the glass state is higher and the flow temperature considerably higher than for the pure polymer. This is due to the strengthening effect of the fillter which is active with respect to the polymer.

PHOSPHORYLATION OF INSOLUBLE POLYMERS

E. B. Trostyanskaya, Lu Syan-zhao, A. S. Tevlina and I. P. Losev, Vysokomol. soedin. **3**: No. 1, 41–45, 1961.

In an investigation of the conditions for the phosphorylation of granular styrene–divinylbenzene copolymer, swelling in phosphorus trichloride, by 180%, it was found that the extent of reaction may attain 93% under conditions analogous to those for phosphorylating alkylbenzenes. The extent of reaction attained in phosphorylating a granulated chloromethylated styrene–divinylbenzene copolymer containing 14·1% chlorine and swelling in phosphorus trichloride by 77% was 72%. In that case substitution of the chlorine atoms corresponded to 79% of the vinylbenzyl chloride units and addition to phenyl groups corresponded to 57% of the styrene units in the copolymer. The insoluble polyelectrolytes obtained with acid numbers 10·2 mg-eq/g and 7·5 mg-eq/g were given the names SF-1 and SF-2 ion exchangers. The apparent dissociation constants of SF-1 ($pK_1=3·4$ and $pK_2=7·2$) and of SF-2 ($pK_1=4·9$ and $pK_2=8·0$) were less than the dissociation constants of the structurally analogous monomeric acids.

THE SPECIFIC EFFECT OF CELLULOSE NITRATE ON THE RADICAL POLYMERIZATION OF SOME VINYL MONOMERS

A. G. Ispravnikova, L. S. Sletkina and Z. A. Rogovin, Vysokomol. soedin. **3**: No. 1, 46–49, 1961.

The possibility of preparing a nitrocellulose-vinylidene chloride graft copolymer has been investigated with the objective of lowering the flammability of cellulose nitrate. A specific influence has been shown to be exerted by the esters of nitric acid (cellulose nitrate, nitroglycerine) on the polymerization of vinylidene chloride and other vinyl monomers. The polymerization of vinylidene chloride and vinyl acetate is considerably retarded by the nitrates, whereas they initiate the polymerization of acrylonitrile.

POLYDIMETHYLSTANNASILOXANES

S. N. Borisov and N. G. Sviridova, Vysokomol. soedin. **3**: No. 1, 50–55, 1961.

Low molecular polydimethylstannasiloxanes containing 2–19% Sn and not described in the literature have been obtained by the joint hydrolysis of dimethyldichlorosilane and dimethyldibromostannane in alkaline medium. Sulphuric acid causes the rupture of the Si–O–Sn bonds of the polymers.

HETEROCHAIN POLYESTERS–XXX. INVESTIGATION OF SOME CORRELATIONS IN THE POLYCONDENSATION OF THE CHLORIDES OF DICARBOXYLIC ACIDS AND DIHYDROXY PHENOLS IN A HIGH BOILING SOLVENT MEDIUM

V. V. Korshak, S. V. Vinogradova, P. M. Valetskii and Yu. V. Mironov, Vysokomol. soedin. **3**: No. 1, 66–71, 1961.

With the polycondensation of terephthalyl chloride and 4, 4′-dihydroxydiphenyl 1-2, 2-propane in a high boiling solvent medium as example a study has been made of the effect

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of such factors as temperature and duration of reaction, solvent species, concentration of the solutions of reactants, molar ratio of the reactants and various additions of molecular weight and yield of the resultant polyarylate. It has been shown that in the polycondensation of terephthalyl chloride with 4, 4′-dihydroxydiphenyl-2, 2-propane the polyarylates with the highest molecular weights are formed at equimolar ratios of the reactants. It is feasible to carry out the polycondensation at 220° and concentration of the reactant solutions 0·6 mole/l.

HETEROCHAIN POLYESTERS—XXXI. INVESTIGATION OF THE CHEMICAL PROPERTIES OF POLYARYLATES

V. V. Korshak, S. V. Vinogradova, P. M. Valetskii and S. N. Salazkin, Vysokomol. soedin. **3**: No. 1, 72–80, 1961.

THE chemical degradation has been investigated of polyarylates of 4, 4′-dihydroxyphenyl-2, 2-propane with isophthalic and terephthalic acids. The polyarylates have been shown to break down at elevated temperatures by the action of 4, 4′-dihydroxyphenyl-2, 2 propane, isophthalic acid and *m*-cresol, but not of isophthalyl chloride. Polyarylates obtained by equilibrium polycondensation are more resistant to chemical degradation than those obtained by interfacial polycondensation. The degradation of polyarylates in *m*-cresol obeys first order relations in the presence of a large access of the cresol. The stability of polyarylates towards acids, alkalis and various organic compounds has been investigated.

MECHANISM OF THE CATALYTIC POLYMERIZATION OF CYCLIC DIMETHYLPOLYSILOXANES—II.

V. N. Gruber and L. S. Mukhina, Vysokomol. soedin. **3**: No. 1, 84–88, 1961.

DIRECTED influence on H_2SO_3 (reduced form of catalyst) oxidation causes a corresponding change in the polymerization rate of cyclic dimethylpolysiloxanes. The polymerization of the latter in the presence of conc. H_2SO_4 and $Al_2(SO_4)_3 . 2H_2O$ as catalysts is accelerated by adding negligible amounts of compounds of varying valency metals ($CuSO_4$, $FeSO_4$, $Fe_2(SO_4)_3$, $MnSO_4$, $KMnO_4$, $Fe(OH_3)$ and ferric naphthenates) and is retarded in the presence of additions of glycerin and ethyl alcohol. The parallism in the action of accelerating and retarding additions on the oxidation of H_2SO_3 and on the polymerization of cyclic dimethylsiloxanes leads to the assumption that the catalytic oxidation-reduction process underlying the polymerization is of a chain nature.

MECHANISM OF THE CATALYTIC POLYMERIZATION OF CYCLIC DIMETHYLPOLYSILOXANES—III

V. N. Gruber, K. V. Nelson, N. V. Kozlova, T. A. Mikhailova and L. S. Mukhina Vysokomol. soedin. **3**: No. 1, 89–92, 1961.

BY quantitative determination of the reduced (H_2SO_3) and peroxide (H_2SO_5) forms of the catalyst (H_2SO_4) it has been shown that both forms coexist in the course of the polymerization of cyclic dimethylpolysiloxanes, evidently as a result of their continuous regeneration during the oxidation-reduction process. With increasing content of linear siloxanes in the polymerizing mass the content of the reduced form decreases and that of the peroxide form increases. IR spectroscopic studies have revealed a direct relation between the content of the peroxide form of the catalyst and the amount of siloxanes of linear structure.

COPOLYMERIZATION OF POLY-1,3-BUTYLENEGLYCOLFUMARATE AND DIETHYLALLYLPHOSPHINIC ACID

M. E. Matkova and S. S. Spasskii, Vysokomol. soedin. **3**: No. 1, 93–98, 1961.

THE copolymerization of poly-1,3,-butyleneglycolfumarate and diethylallylphosphinic acid has been investigated. The reactivity constants of the system have been determined to

be $r_1 = 9{\cdot}25 \pm 3{\cdot}00$ and $r_2 = 0{\cdot}12 \pm 0{\cdot}008$. It has been shown that formation of crosslinked copolymers of the polyesters with the allylic derivatives of acids of phosphorus takes place as a result of the reaction of the polyester units both with the monomer as well as with each other. The mechanical and dielectric properties of the poly-1,3-butyleneglycolfumarate —diethylallylphosphinic acid copolymers have been determined.

ABSORPTION AND LUMINESCENCE SPECTRAL STUDY OF DYE-POLYELECTROLYTE INTERACTION IN SOLUTIONS—I. AQUEOUS SOLUTIONS OF RHODAMINE 6G IN THE PRESENCE OF METHACRYLIC ACID

M. A. Katibnikov and I. N. Ermolenko, Vysokomol. soedin. **3**: No. 1, 105–112, 1961.

A STUDY has been made of the absorption and luminescence spectra and of the intensity and polarization of luminescence of aqueous solutions of rhodamine 6G in the presence of polymethacrylic acid. With increase in polymethacrylic acid concentration up to a certain value an increase takes place in the short wave length peak of the absorption spectrum and a sharp fall in intensity of the luminescence. Further addition of the polyelectrolyte leads to a flare-up of luminescence, to a growth in the long wavelength peak of the absorption spectrum and to a sharp increase in the degree of polarization of the luminescence. This is explained on the basis of the formation and breakdown of luminescent and non-luminescent joint aggregates of dye and polymer as the concentration of polymethacrylic acid changes.

STRENGTH, DEFORMATIVE AND VISCOUS PROPERTIES OF ACRYLONITRILE RUBBER SOLUTIONS IN TOLUENE-DECALIN SOLVENT AT HIGH DEFORMATION RATES

T. I. Zatsepina and A. A. Trapeznikov, Vysokomol. soedin. **3**: No. 1, 113–121, 1961.

THE effect of solvent (toluene) - non-solvent (decalin) mixture on the structure and mechanical properties of concentrated acrylonitrile rubber SKN-18 solutions has been investigated. The investigation was carried out in the range of high deformation rates (36–1100 sec^{-1}) on an elastorelaxometer by a constant deformation rate technique. It has been shown that on addition of decalin the degree of structuration of the solutions increases owing to intensification of the intermolecular interactions of the rubber. This leads to a growth in the ultimate high elastic deformation, structural strength and viscosity. For a 1:1 decalin–toluene ratio the above characteristics exhibit a maximum. Excess decalin above the 1:1 ratio lowers the value of the characteristics, which is explained by excess intermolecular links, leading to microcoagulation of the rubber. It has been found that the maximum high elastic deformation and structural strength values of the rubber determined at high deformation rates are sensitive indicators of structural changes of the systems.

SYNTHESIS OF GLYCINE-IMINO ACID PEPTIDE ANALOGUES OF A COLLAGEN FRAGMENT

K. T. Poroshin, V. A. Shibnev, T. D. Kozarenko and V. G. Debabov, Vysokomol. soedin. **3**: No. 1, 122–130, 1961.

HEXA-, nona- and dodecapeptide derivatives with the sequence gly-pro-X, where X is proline or hydroxyproline, as possible fragments of a collagen molecule, have been synthesized by the mixed anhydride method. It was found that collagenase very weakly hydrolyses

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nona- and decapeptide and therefore the assumption has been advanced that the occurrence of such a sequence in the protein is of little probability. It has been assumed on the basis of a number of data that more probable is the sequence consisting of the alternating fragment—gly-pro-hydroxypro-gly—which may serve as the source of formation both in the tripeptide gly-pro-hydroxypro as well as of glycine during hydrolysis by collagenase. Collagen-like reflexes could not be obtained on X-ray structural analysis of the peptides and the change in value of the specific rotation of the peptides as the amount of iminoacids increases does not have the nature of a linear relationship.

ON THE ASYMMETRY OF CRITICAL OPALESCENCE

V. S. Skazka, Vysokomol. soedin. **3**: No. 1, 131–133, 1961.

THE asymmetry of critical opalescence of cyclohexane solutions of the polystyrene fraction $M+2.8=10^5$ has been investigated as function of the concentration. The Debye equation for the dependence of the light scattering intensity upon scattering angle holds for the critical concentration $c_k=3\%$. The sizes of the molecules calculated from the asymmetry of the critical opalescence coincide with those calculated from viscometric measurements.

SYNTHESIS AND POLYMERIZATION KINETICS OF VINYL SALYCILATE

D. Hardy, V. Spiegel and K. Nytrai, Vysokomol. soedin. **3**: No. 1, 144–149, 1961.

VINYL salycilate has been synthesized by transesterification of vinyl acetate with salycilic acid. The kinetics of the azo-*bis*-isobutyronitrile initiated polymerization of vinyl salycilate have been investigated and the chain transfer constant of the monomer molecule ($C_M=8{\cdot}0\times$ $\times10^{-3}$ at 70°) and over-all activation energy of the polymerization reaction ($E=27{\cdot}7$ kcal/mole) have been calculated.

EFFECT OF TEMPERATURE ON THE LIFETIME OF RUBBERS UNDERGOING CORROSIVE CRACKING

Yu. S. Zuev, A. Z. Borshchervskaya, S. I. Pravednikova and U Yue-tzin, Vysokomol. soedin. **3**: No. 2, 164–173, 1961.

THE rate of reaction of underformed rubber with an aggressive medium is determined by the diffusion of the latter in the polymer, whereas the rate of destruction of deformed rubber is determined both by the value of the stress and the rate of chemical reaction with the medium. The apparent activation energy of the rupture (u) of the rubber depends on the type of bonds undergoing breaking, as well as upon the ability of the aggressive medium to be adsorbed on the rubber. For a given rubber-medium system the u values are about equal in the region of small deformations and increase on passing over to deformations of 500–700%. The dependence of the time for the rupture upon the deformation in an aggressive medium is expressed by a curve with an extremum, the position of the minimum (ε_{cr}) depending upon the temperature, type of aggressor and physical state of the medium (gas, solution). Owing to the shift in ε_{cr} with change in temperature in the region of a certain deformation one may observe an anomalous temperature dependence of the rupture time.

MECHANISM OF THE CATALYTIC POLYMERIZATION OF CYCLIC DIMETHYLPOLYSILOXANES—IV

V. N. Gruber and L. S. Mukhina, Vysokomol. soedin. **3**: No. 2, 174–176, 1961.

THE well known oxidation-reduction system: $2KMnO_4+3H_2SO_4=2MnSO_4+K_2SO_4+$ $+3H_2O+2{\cdot}5\ O_2$ employed as catalyst caused the polymerization of cyclic dimethylpoly-

siloxanes, leading to the formation of a rubber-like polymer (siloxane rubber). This confirms the earlier view that the catalytic polymerization of cyclic dimethylsiloxanes is brought about by oxidation-reduction reactions undergone by the catalysts (conc. H_2SO_4, $FeCl_3$).

THE SWELLING OF ION EXCHANGE RESINS IN MIXED SOLVENTS

G. M. Panchenkov and V. I. Gorshkov, Vysokomol. soedin. **3**: No. 2, 177–183, 1961.

AN experimental investigation has been made of the swelling of the cation exchangers SDV-3, SBS, KU-1, KB-4P-2 in aqueous acetone solutions. The dependence of the swelling upon the solvent composition is different for the various resins and is determined by the type of exchange groups, the capacity, the cationic form of the resin and the structure of its hydrocarbon skeleton. For the various salt forms of the resins (accepting the hydrogen form of the carboxyl resin KB-4P-2) in the solvents the following swelling relation has been found: H-form > Li-form > Na-form > K-form. The resins selectively sorb water from solutions with a high concentration of the organic component.

HETEROCHAIN POLYAMIDES—XXVIII. ON THE SIGNIFICANCE OF HYDROCHLORIC ACID ACCEPTORS IN THE SYNTHESIS OF POLYAMIDES BY INTERFACIAL POLYCONDENSATION

V. V. Korshak, T. M. Frunze, V, V. Kurashev and K. L. Serova. Vysokomol. soedin. **3**: No. 2, 205–207, 1961.

THE effect of the nature and concentration of acid acceptors (KOH, Na_2CO_3 and C_5H_5N) on the synthesis of polyhexamethyleneadipamide by interfacial condensation has been investigated. It has been found that the highest yield and molecular weight of the polyamides are obtained at an acceptor-diamine ratio of 2 for KOH, and 4 for Na_2CO_3. An increase in the amount of pyridine in the reaction medium leads to a fall in yield and in the molecular weight of the polymer.

THERMOMECHANICAL INVESTIGATION OF POLYDIPHENYLSILOXANEETHYLENEFUMARATE-STYRENE COPOLYMERS

M. A. Bulatov and S. S. Spasskii, Vysokomol. soedin. **3**: No. 2, 208–212, 1961.

IN the alcoholysis of diphenyldiethoxysilane by low molecular polyethyleneglycolfumarate an unsaturated polyester containing diphenylsiloxane chains in the backbone has been obtained. It has been shown thermomechanically that the incorporation of silicon in the form of difunctional units in the polyester chain lends elasticity to copolymers of the polyesters with styrene. The elastic deformation is minimal in copolymers approaching an azeotropic composition. The nature of hydrocarbon radicals at the silicon atom does not affect the relative activity of the fumaric bond in the copolymerization reaction with styrene.

EFFECT OF MOLECULAR WEIGHT ON THE STRENGTH OF ORIENTED AMORPHOUS POLYMERS

L. A. Laius and E. V. Kuvshinskii, Vysokomol. soedin. **3**: No. 2, 215–222, 1961.

STRETCH curves have been obtained for films of polyvinylacetate, polystyrene and polymethylmethacrylate specimens of various molecular weights, preliminarily subjected to

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varying degrees of drawing at elevated temperatures. The strength at first sharply increases with increase in orientation, then the increase becomes less and finally stops altogether. In a number of cases there is a fall in strength on further drawing. In the region of relatively high molecular weights (for example, for polyvinylacetate $M_v = 0{\cdot}15 \times 10^6$–$0{\cdot}45 \times 10^6$) the strength of the unoriented specimens remains practically constant or changes very little with the molecular weight. The strength of the oriented specimens continues to increase markedly with increase in molecular weight, attaining very high values (for example, in the case of polyvinylacetate $\sigma_p \sim 4000$ kg/cm^2).

THE ACTION OF GAMMA RAYS ON THE STRUCTURE OF CELLULOSE FIBRES

Kh. U. Usmanov, E. I. Kalabanovskaya and R. B. Damovskii, Vysokomol. soedin. **3**: No. 2, 223–227, 1961.

The integral heats of wetting by water have been determined of cotton and viscose fibres irradiated by γ-rays in air, nitrogen and vacuum with doses from 5×10^4 to 5×10^7 roentgens. It has been shown that in the irradiation process the cellulose acquires a looser structure. The heats of wetting increase on passing from vacuum to air as irradiation medium, owing to increase in the oxidative degradation of the cellulose. The more closely packed hydrocellulose is less sensitive to the action of γ-rays than is natural cellulose. The loosening of the cellulose packing effected by radiation has been shown to be a reversible process and that in the course of a year the irradiated and, as a result, degraded cellulose with greatly loosened structure relaxes with reversion to the dense packing.

DETERMINATION OF THE DIFFUSION COEFFICIENT OF POLYPARACHLOROSTYRENE FRACTIONS IN CHLOROFORM

K. G. Berdnikova and K. A. Aslanyan, Vysokomol. soedin. **3**: No. 2, 228–231, 1961.

Diffusion and viscosity of chloroform solutions of polyparachlorostyrene have been determined. Correlations have been obtained between the diffusion coefficient D and intrinsic viscosity $[\eta]$ and the molecular weight. The statistical lengths of the polyparachlorostyrene molecules in chloroform have been calculated. The experimental data obtained lead to the conclusion that the polyparachlorostyrene fractions investigated obey the laws holding for linear macromolecules.

CHANGE IN THE STRENGTH OF CARBOXYLIC CATION EXCHANGERS IN AQUEOUS ORGANIC MEDIA

Lou Chi-syan, E. M. Savitskaya and B. P. Bruns, Vysokomol. soedin. **3**: No. 2, 237–243, 1961.

Potentiometric titration curves have been obtained of a carboxylic cation exchange polymer in aqueous methanol mixtures of varying composition. It has been found that as the methanol concentration in the solution increases the dissociation constant of the acid-exchanger falls. The negative logarithm of the apparent dissociation constant of the exchanger has been shown to increase linearly with increase in value of the reciprocal dielectric constant of the medium. A new rapid method of titrating carboxylic resins in mixed and non-aqueous media has been developed.

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POLYMERIZATION OF N-SUBSTITUTED METHACRYLAMIDES—III. N, N-DISUBSTITUTED METHACRYLAMIDES

T. A. Sokolova and G. M. Chetyrkina, Vysokomol. soedin. **3**: No. 2, 244–247, 1961.

A NUMBER of N, N-disubstituted methacrylamides have been synthesized, of which methyl-*o*-, *p*- and *m*-ethoxyphenylmethacrylamides have been synthesized and characterized for the first time. It has been shown that N, N-disubstituted methacrylamides do not polymerize under conditions of radical polymerization. Dimethyl-, diethyl-, diphenyl-, methylphenyl- and piperidylmethacrylamides form viscous liquids on irradiation by ultraviolet light in the presence of BF_3. Some of the compounds synthesized copolymerize with methylmethacrylate and styrene. It has been proposed that the absence of ability for radical polymerization among N, N-disubstituted methacrylamides is due to steric hindrances.

POLYMERIZATION OF α-ACYLAMINOACRYLIC ACIDS

S. S. Ivanov and M. M. Koton, Vysokomol. soedin. **3**: No. 2, 248–254, 1961.

A DESCRIPTION has been made of the polymerization of α-acylaminoacrylic acids ($CH_2=C(NHCOR)COOH$ where R = H, CH_3, C_6H_5-, $C_6H_5CH_2-$, $C_6H_5CH_2-O-$ in dimethylformamide solution in the presence of azoisobutyrodinitrile at 50, 60 and 70° and for R = C_6H_5-, $C_6H_5CH_2-$, and $C_6H_5CH_2-O-$ also in dioxane solution with the same initiator at 70°. Transparent, colourless or slightly brown polymers were obtained, soluble in dimethylformamide but insoluble in the majority of the common organic solvents. The polymerization kinetics of the acids and thermal degradation kinetics of the polymers were investigated. A proposal has been made as to the direction of the degradation process.

INVESTIGATION OF THE VULCANIZATION OF POLYCHLOROPRENE LATEXES—II. SULPHONATION

D. M. Sandomirskii and E. M. Spektor, Vysokomol. soedin. **3**: No. 2, 255–261, 1961.

THE interaction of polychloroprene latexes with alkaline metal polysulphides (sulphonation) has been studied at room and elevated temperatures. It has been found that the polymer reacts both with the polysulphide itself as well as with alkaline metal thiosulphate accompanying the latter. In the first case the polymer is structurized by chains consisting of 5 sulphur atoms, in the second the Bunte polymer salt is formed. Structuration of the polymer proceeds further during the subsequent chemical conversions of the addition products, leading to noticeable improvement of the frost resistance of the films as determined by the T-50 method. The polymer reacts with the polysulphides due to its possessing a small amount of allyl (labile) chlorine. Addition of sulphur ceases on consumption of the allylic chlorine.

POLYMERIZATION OF ALDEHYDES UNDER HIGH PRESSURES—I. POLYMERIZATION OF BUTYRALDEHYDE UNDER PRESSURE

V. M. Zhulin and M. G. Gonikberg, Vysokomol. soedin. **3**: No. 2, 262–267, 1961.

AT room temperature butyraldehyde polymerizes only at pressures above about 5000 kg/cm² and the reaction proceeds with an induction period. Addition of benzoyl peroxide

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increases the polymerization rate and lowers the molecular weight of the polymers. Under the conditions studied azo *bis* isobutyronitrile has no marked influence upon the polymerization reaction; the latter is inhibited by hydroquinone.

The drop in rate of thermal depolymerization of unstable polybutyraldehyde caused by hydroquinone or quinone indicates a radical chain mechanism of this process.

POLYMERIZATION OF ALDEHYDES UNDER HIGH PRESSURES—II. ON THE MECHANISM OF BUTYRALDEHYDE POLYMERIZATION UNDER PRESSURE

M. G. Gonikberg and V. M. Zhulin, Vysokomol. soedin. **3**: No. 2, 268–275, 1961.

DATA were obtained in favour of a radical chain mechanism for butyraldehyde polymerization at ~6000 kg/cm² and room temperature. In the presence of organic acids under the above conditions parabutyraldehyde is formed from butyraldehyde. Parabutyraldehyde inhibits polymerization of butyraldehyde to solid polymers.

In the presence of triethylamine under pressure no polymerization takes place because of aldol condensation of butyraldehyde. Addition of water and propanol leads to the formation of very low molecular weight polymers of butyraldehyde.

TEMPERATURE DEPENDENCE OF FLOW BIREFRINGENCE OF POLYMER SOLUTIONS IN AN "IDEAL SOLVENT"

E. V. Frisman and Syui Mao, Vysokomol. soedin. **3**: No. 2, 276–284, 1961.

THE flow birefringence, birefringence in the electrical field and viscosity of the system, polystyrene—cyclohexane have been studied as function of temperature. The experimental data showed that near the critical temperature of solution in solutions of finite concentration aggregates are formed that introduce a very large form effect in the flow birefringence. The optical anisotropy of the "aggregation" does not differ from that of the macromolecules. The existence of "aggregation" does not affect the rotational mobility of the units in the electrical field. At infinite dilution the solution acts as ideal over the entire temperature range investigated.

FLOW BIREFRINGENCE AND VISCOSITY OF THE SYSTEM POLYISOBUTYLENE—BENZENE NEAR THE CRITICAL SOLUTION TEMPERATURE

E. V. Frisman and Syui Mao, Vysokomol. soedin. **3**: No. 2, 285–289, 1961.

THE temperature dependence of the flow birefringence and viscosity of the system polyisobutylene—benzene has shown that "aggregation" of the macromolecules takes place near the critical temperature of solution. The optical anisotropy of the "aggregates" themselves does not differ from that of the macromolecules. This is because the anisotropy of the macromolecules is independent of the molecular weight. In the case of systems with the form effect, the total anisotropy undergoes an enormous change near the critical temperature, which is explained by the dependence of the form anisotropy on the molecular weight of the particles under question.

PEROXIDE INDUCED CROSSLINKING IN POLYETHYLENE

R. Rado and M. Lazar, Vysokomol. soedin. **3**: No. 2, 310–318, 1961.

THE mechanism of the reaction which leads to polymer crosslinking was deduced from kinetic analyses of benzoyl peroxide decomposition, crosslinking and secondary reaction products. Crosslinks between polyethylene macromolecules were found to be formed in consequence of polymer-radicals recombination. In polyethylene, benzoyl peroxide decomposes by

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a chain mechanism with a second order induced decomposition reaction caused by interaction of benzoyloxy radicals with benzoyl peroxide. Termination is effected partly by recombination of two polymer radicals, partly by desactivation between benzoyloxy and macro-radicals. The most important role is played by the elementary transfer step, which determines the yield of crosslinks. The rate of crosslinking is generally equal to the rate of that part of spontaneous cleavage which is equivalent to polymer-radical recombination.

ON THE EFFECT OF THE NATURE OF THE MEDIUM AND OF THE CATALYST ON CATALYTIC COPOLYMERIZATION

S. P. Mitsengendler, N. N. Ivanov and A. A. Korotkov, Vysokomol. soedin. **3**: *No. 2, 319, 1961.*

In this letter the following erroneous conclusions in the paper [1] have been indicated: in the case of *p*-chlorostyrene (A) and styrene (B) the composition of the γ-radiation polymer does not coincide with that of the radical polymer. A=36% and 54·5% respectively. In the copolymerization of A and B by sodium naphthalate the content of A is 63·5% instead of 81%. By lowering the temperature to −30 and −78° one may attain yields of polymer A up to 50 and 100% respectively.

THE CHEMICAL NATURE OF N-VINYLACETAMIDE DESCRIBED BY BACSKAI AND HALMOS

A. A. Vansheidt, S. S. Skorokhodov, S. G. Ershova and N. V. Mikhailova, Vysokomol. soedin. **3**: No. 2, 320, 1961.

It has been pointed out that the dehydrochlorination of N-β-chloroethyl derivatives is inapplicable for the synthesis of secondary N-vinylamides.

GAMMA RAY INDUCED LOW-TEMPERATURE LIQUID-PHASE POLYMERIZATION OF TETRAFLUOROETHYLENE

A. R. Gantmakher, S. S. Medvedev and A. D. Abkin, Vysokomol. soedin. **3**: No. 2, 320, 1961.

It has been shown that the low-temperature liquid-phase polymerization of tetrafluoroethylene proceeds at a high rate.

INVESTIGATION OF MOLECULAR INTERACTION IN SOLUTIONS OF POLYMERS BY THEIR CONVERSION TO THE COLLOIDAL SYSTEM

S. A. Glikman, E. P. Korchagina and L. L. Sevyants, Vysokomol. soedin. **3**: No. 3, 353,–358 1961.

The degree of dispersity of sols obtained during the rapid mixing of highly dilute polymer solutions with excess non-solvent is directly related to the degree of association of the polymer molecules in the initial solutions. The size of the resultant colloidal particles depends upon the molecular weight of the polymer, upon its concentration in the initial solution and upon the mixing temperature. In ultimately dilute solutions the polymer molecules are practically non-associated and the particles of the sols produced from them are coiled

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single molecules. The stability of the sols with time is determined by the adsorption by the disperse phase particles of low molecular impurities contained in the initial polymer. On conversion of solutions of sufficient concentration it has been found possible to seperate the disperse phase into gel and sol fractions. The former formed from large associates contains molecules of a higher degree of polymerization; the latter formed of lesser associates and of single molecules contains molecules of lesser degree of polymerization. This novel principle has been successfully employed to fractionate a number of polymers.

A STUDY OF THE INHOMOGENEITY OF COTTON CELLULOSE

T. I. Sushkevich and Kh. U. Usmanov, Vysokomol. soedin. **3**: No. 3, 359–362, 1961.

THE molecular weight distribution of cotton cellulose in the growing season of the cotton plant has been investigated by fractional precipitation of the cellulose nitrates. The distribution curves exhibit a maximum that increases in length, becomes narrower and shifts in the direction of higher molecular weights with ageing of the fibre. It thus follows that ripening of the fibre is accompanied by decrease in molecular inhomogeneity of the cellulose.

SYNTHESIS AND POLYMERIZATION OF METHYL-α-METHOXYACRYLATE

S. S. Ivanov, Vysokomol. soedin. **3**: No. 3, 368–370, 1961.

WITH the object of investigating the polymerizability of methyl-α-methoxyacrylate and the properties of the polymer the monomer was synthesized both by Baker's and by Claisen's methods. Benzoyl peroxide-and azoisobutyronitrile-initiated block polymerization in a nitrogen atmosphere yielded a transparent glassy material of slightly brown colour. A number of physical and chemical properties of the polymer has been presented. The bulk polymerization kinetics of methyl-α-methoxymethactylate in the presence of azoisobutyronitrile in nitrogen atmosphere has been investigated at 50, 60 and 70°. Thermal stability data of the polymer up to 225° have been presented.

SYNTHESIS OF NEW CELLULOSE AND OTHER POLYSACCHARIDE DERIVATIVES—XII. DEVELOPMENT OF A METHOD FOR THE INTERFACIAL ESTERIFICATION OF CELLULOSE

Sun' Tun, John Vey-gan and Z. A. Rogovin, Vysokomol. soedin. **3**: No. 3, 382–389, 1961.

A METHOD of interfacial esterification of cellulose has been developed, based on the interaction of water or alkali soluble cellulose derivatives with an acylchloride solution in a non-polar solvent. The effect of the chemical structure of the acyl chloride and of the polysaccharide on the conditions of esterification and the degree of substitution of the resultant ester has been elucidated.

POLYMERIZATION OF METHYLMETHACRYLATE IN THE PRESENCE OF THE SYSTEM ORGANIC ACID—DIMETHYLANILINE—I

M. F. Margaritova and S. D. Evstratova, Vysokomol. soedin. **3**: No. 3, 390–391, 1961.

IN harmony with Yui Tsyao's data the possibility has been confirmed of initiating polymerization by the system organic acid—dimethylaniline. The results of the bulk polymerization of methyl methacrylate in the presence of this system showed that the polymerization

rate increases with the dissociation constant of the acid, the process proceeding by a radical mechanism. A possible mechanism for the initiation has been suggested.

POLYMERIZATION OF METHYLMETHACRYLATE IN THE PRESENCE OF THE SYSTEM ORGANIC ACID—DIMETHYLANILINE—II

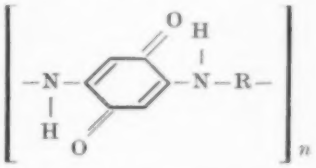
M. F. Margaritova and S. D. Evstratova, Vysokomol. soedin 3: No. 3, 398–401, 1961.

GENERAL correlations of the "dark" and ultraviolet induced polymerization of methyl methacrylate (MMA) in the presence of benzoic acid (BA) and dimethylaniline (DMA) have been ilusidated. The emulsion polymerization of MMA in the presence of BA + DMA proceeds at considerable speed already at 30°. Increase in pH of the medium lowers the emulsion polymerization velocity.

POLYMERS WITH A CONJUGATED BOND SYSTEM AND HETEROATOMS IN THE CONJUGATE CHAIN—XII. THE SYNTHESIS AND PROPERTIES OF SOME POLYAMINOQUINONES

V. P. Parini, Z. S. Kazakova, M. N. Okorokova and A. A. Berlin, Vysokomol. soedin. **3**: No. 3, 402–407, 1961.

POLYAMINOQUINONES of the probable formula



where R = $(CH_2)_6$, C_6H_4, $C_{12}H_8$, $C_{12}H_6(COOH)_2$ were synthesized by the interaction of *p*-benzoquinone with hexamethylenediamine, *p*-phenylenediamine, benzidine and benzidine-3,3′-dicarboxylic acid. The resultant compounds are non-fusible, possess electron-exchange properties and give intense electron resonance signals. The polymers obtained from aromatic diamines are thermostable. The polymer prepared with benzidine dicarboxylic acid was characterized by somewhat enhanced electroconductivity (of the order of 10^{-10} $ohm^{-1}cm^{-1}$). On interaction with copper salts in solution it yields an insoluble salt, presumably of the type of crosslinked chelate polymers.

PHOSPHONITRILECHLORIDE RUBBER PNC

S. M. Zhivukhin, V. B. Tolstoguzor and Yu. V. Meitin, Vysokomol. soedin. **3**: No. 3, 414–419, 1961.

THE ageing mechanism of phosphonitrilechloride rubber has been discussed. The phenomenon was studied by a number of methods. It was found that the ageing is due to two processes: (1) crytallization of the PNC rubber and (2) hydrolysis of the P—Cl bonds with the formation of P—O—P links; crosslinking and concurrent degradation thus taking place. In the IR spectra a shift in the absorption bends corresponding to the P=N bond towards the shorter wavelength region has been noted with increase in degree of polymerization (MW from 2×10^3 to 1×10^6).

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LIGHTSCATTERING AND VISCOSITY OF DICHLORO-SUBSTITUTED POLYSTYRENE IN AN IDEAL SOLVENT—II. POLY-3,4-DICHLOROSTYRENE

V. E. Eskin and L. N. Andreeva, Vysokomol. soedin. **3**: No. 3, 435–440, 1961.

THE light scattering and viscosity of 8 poly-3,4-dichlorosterene fractions (M from $0{\cdot}4\times10^6$) in an ideal solvent have been measured. The molecular weights and unperturbed sizes of the coils have been measured. The latter are 25% greater than the coils of polystyrene and poly-2,5-dichlorostyrene of the same degree of polymerization. The reason for the decrease in flexibility of the poly-3,4-dichlorostyrene molecule is apparently the electrostatic interaction of its polar side chains.

TIME-TEMPERATURE DEFENDENCE OF STRENGTH OF POLYMER FIBRES—I

S. N. Zhurkov and S. A. Abasov, Vysokomol. soedin. **3**: No. 3, 441–449, 1961.

THE time-temperature dependence of the tensile strength of viscose, capron, polypropylene, nitrile and chlorovinyl fibres has been investigated over the temperature range 150–120°C. It has been shown that the experimental data are in good agreement with the equation: $\tau=\tau_0\exp(u_0-\gamma\sigma/kT)$. According to the equation the fibre life τ decreases exponentially with increase in stretching stress σ and absolute temperature T. The constants τ_0, u_0 and γ, determining the strength of the fibre, have been calculated. The pre-exponential factor τ_0 has been found to possess the same order of value for all the fibres investigated, namely 10^{-12}–10^{-3} sec. The coefficient u_0 determining the activation energy of the breakdown of the polymer fibres corresponds to chemical bond energy. The factor γ of the dimensions of volume was found to be highly susceptible to changes in the structure of the fibres. An activation mechanism of polymer rupture has been suggested. This is conceived of as a process developing in time under the action of temperature and mechanical stress.

THE ROLE OF CHEMICAL AND INTERMOLECULAR BONDS IN POLYMER RUPTURE

S. N. Zhurkov and S. A. Abasow, Vysokomol. soedin. **3**: No. 3, 450–455, 1961.

THE change in the time-temperature relation of the strength of viscose, capron and polyacrylonitrile fibres has been investigated as function of orientation and plasticization. It has been shown that strengthening of the fibres on orientation and weakening on plasticization is reflected by change in the structure-susceptible coefficient γ in the equation $\tau=\tau_0\exp(u_0-\gamma\sigma)/kT$. The activation energy of rupture u_0 for fibres of varying strength has been found to be independent of the intermolecular bonds and not to change with orientation and plasticization. From this it has been concluded that the strength of polymer fibres is associated with rupture of chemical bonds. Molecular interaction affects the strength indirectly, through the coefficient γ.

CARBOCHAIN POLYMERS AND COPOLYMERS—XXX. COPOLYMERIZATION OF VINYLSULPHOFLUORIDE

E. F. Rodionova, H. S. Kolesnikov, L. Z. Soborovskii and B. M. Gladshtein, Vysokomol. soedin. **3**: No. 3, 456–458, 1961.

VINYLSULPHOFLUORIDE has been shown to block copolymerize with styrene, methylmethacrylate, vinyl acetate and acrylonitrile in the presence of azobisisobutyronitrile. The copolymerization of vinylsulphofluoride with styrene has been investigated and the effect has been shown of the initial monomer mixture on the composition and properties of the copolymers.

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CARBOCHAIN POLYMERS AND COPOLYMERS—XXXI. POLYMERIZATION AND COPOLYMERIZATION OF VINYLPHOSPHINYL CHLORIDE

E. F. Rodionova and H. S. Kolesnikov, Vysokomol. soedin. **3**: No. 3, 459–463, 1961.

VINYLPHOSPHINYL chloride has been shown to undergo radical polymerization and to copolymerize with methyl methacrylate, styrene and vinyl acetate. The properties of the resultant polymers have been investigated and it has been shown that by the action of water on vinylphosphinyl chloridemethyl methacrylate copolymers vinylphosphinic acid-methyl methacrylate copolymers are formed. The latter possess elevated softening temperatures, apparently due to formation of hydrogen bonds between the polymer molecules. Saponification of the vinylphosphinyl chloride-vinyl acetate copolymer yields a vinylphosphinic acid-vinyl alcohol copolymer, soluble in water.

OXIDATION OF HYDROCARBONS IN THE PRESENCE OF INHIBITORS

D. Rysavy, Vysokomol. soedin. **3**: No. 3, 464–469, 1961.

OXIDATION of isotactic polypropylene in the presence of an antioxidant has been studied. Examination of the length of the inhibition period in relation to the concentration of phenyl-2-naphthylamine revealed the existence of a critical concentration of the anti-oxidant, previously postulated by N.N. Semenov. For concentrations above the critical an equation has been derived expressing the length of the inhibition period as function of the intitial antioxidant concentration. Ratios of the elementary growth growth and termination constants ($6{\cdot}0 \times 10^{-4}$ to $7{\cdot}6 \times 10^{-4}$) and the activation energy difference of these reactions have been determined from the critical concentrations for temperatures between 160 and 180°C. An increase in antioxidant concentration to over 0·5% results in a shortening of the inhibition period.

CLASSIFICATION OF GRAFT COPOLYMERS

H. S. Kolesnikov and Tsen Khan-min, Vysokomol. soedin. **3**: No. 3, 475–476, 1961.

A CLASSIFICATION of graft copolymers based on the chemical structure principle has been proposed. The classification makes it possible to note in the name of the copolymer the chemico-structural and structural characteristics of the polymer backbone and of the side chains.

LAEVOGLUCOSAN POLYETHERS—I. POLYMERIZATION OF LAEVOGLUCOSAN AND ITS ETHERS

V. V. Korshak, O. P. Golova, V. A. Sergeev, N. M. Merlis, R. Ya. Shneer, Vysokomol. soedin. **3**: No., 3, 477–485, 1961.

POLYMERIZATION of laevoglucosan and of its ethers, leading to high molecular weight polymers has been described. The most efficient catalysts for the reaction were shown to be boron fluoride etherates, ferric chloride and aluminum chloride. Owing to the presence of free secondary hydroxyl groups chain transfer reactions take place to a considerable extent during the process, leading to the formation of amorphous and evedintly branched

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polymers. In the case of polymerization of trimethyllaevoglucosan the resultant polymer is crystalline and evidently of linear structure. Polymerization of laevoglucosan with the formation of polymers of molecular weight 20,000–60,000 is carried out at 90—100° in absolute dioxane. Polymerization of trimethyllaevoglucosan leading to polymers of molecular weight 250,000—400,000 is carried out at 20° in absolute toluene. A mechanism has been proposed for the polymerization of trimethylglucosan and a discussion presented of the polymerization mechanism of laevoglucosan.

CRYSTALLINITY OF THE HYDROGENATION PRODUCTS OF CIS-1,4-POLYBUTADIENE

B. I. Tikhomirov, A. I. Yakubchik and I. A. Klopotova, Vysokomol. soedin. **3**: No. 3, 486, 1961.

X-RAY analysis bears evidence of the crystallinity of hydrogenation products of *cis*-1,4-polybutadiene with degree of unsaturation 70% and lower. The products are capable of spherulite formation.

ADDITION OF UNSATURATED COMPOUNDS TO DIMETHYLMETHYL POLYSILOXANES

V. O. Reikhsfeld and A. I. Bondarenko, Vysokomol. soedin. **3**: No. 3, 486–487, 1961.

IT has been shown that in principle organosilicon compounds may be modified by the addition of vinyl monomers to the Si—H bonds, existing in the initial polysiloxanes.

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